

ELECTROCHROMIC AND THERMOCHROMIC MATERIALS
FOR SOLAR ENERGY APPLICATIONS WITH EMPHASIS
ON NIOBIUM AND VANADIUM OXIDES

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FOR SOLAR ENERGY APPLICATIONS WITH EMPHASIS ON NIOBIUM
AND VANADIUM OXIDES

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BACKGROUND

Materials are known as chromogenic when they change their color in response to some stimulus. In thermochromic (TC), electrochromic (EC) and photochromic (PC) materials the stimuli are temperature, electric field and photons respectively. Scientists at the Energy Efficient Buildings Program at the Lawrence Berkeley Laboratory, University of California have led the efforts to study the solar energy applications of these materials. (Refs. 1-4). The objectives of this program were to investigate the literature, analyze and report on the properties of EC and TC materials that may be useful for solar energy conversion and building glazing applications. The intent was to emphasize, but not limit the study to, the oxides of vanadium and niobium.

Materials for use in building glazing applications have to perform in the -30°C to 40°C range and they have to be nonlinear with respect to solar energy transmittance. A similar performance except for operation at much higher temperatures (up to 300°C) would be of interest in solar collector glazing. Also of interest is a material that can operate up to 600°C and switch between being a solar absorber and reflector.

APPROACH

The Honeywell Systems and Research Center (HSRC) approach to conducting this literature study of EC and TC materials for solar energy applications was as follows:

- o Extract applicable data from papers already in HSRC files
- o Collect additional papers from references in the papers on file

- o Conduct computerized literature searches through DIALOG (COMPENDEX, INSPEC and NTIS), DTIC/DROLS and NASA/RECON, in order to develop additional references for relevant materials. These databases are available through the HSRC Information Center.
- o Develop a matrix (materials vs. properties) for all the materials that exhibit nonlinear behavior. The properties of interest were those that have importance related to the specific applications of the subject program. A great many of the cells in the matrix remain empty, mostly because no data has been published, at least in the available databases. Materials have been included in the Tables even though they do not seem applicable now.
- o Write discussions of those nonlinear materials that appear to be the best candidates for nonlinear solar energy applications.
- o Generate recommendations for additional experimental work to develop the most promising materials for use in solar energy applications.

THERMOCHROMIC MATERIALS

INTRODUCTION

Materials that undergo a color transition at a specific temperature (thermochromic) could be used as passive switches on building glazing. For example, a coating of TC material on window glass would hypothetically perform as follows: When the coating (glass) is below the transition temperature (T_t), it will transmit solar energy quite well. As the coating heats up (air temperature, coating absorptance, solar flux) through T_t it switches to a metallic state and reflects the IR solar radiation, thus allowing a lower influx of solar energy through the window. In the case of vanadium dioxide

(VO₂), at 2.5 μm , the influx can be reduced by a factor of 100 or more for a film of at least 350nm thickness. That factor decreases with wavelength and there are evidences that in the very near IR and part of the visible spectrum, the transmittance might even increase. As the solar flux seen by the coating decreases, or if the outside air temperature decreases, the coating will cool through T_t and allow a higher percentage of the incident solar flux to pass through.

The following section discusses the available stoichiometric materials and shows that there are none that switch at an applicable temperature. The following discussion covers doping of these materials and introducing other effects that shift their transition temperatures, and that is followed by a discussion of the issues related to using these materials for building glazing applications.

STOICHIOMETRIC COMPOUNDS

The most common of the thermochromic (TC) materials are crystalline transition metal compounds, predominantly the oxides of vanadium and titanium. Figure 1 (from Ref. 5) shows the electrical conductivity as a function of inverse temperature for several of these transition metal compounds. We have added a shaded area (a) that shows the temperature range within which switching would have to occur for application to building glazings. We have also indicated the temperatures below which solar collector glazings and absorbers would have to switch (B and C, respectively). It immediately becomes apparent that none of the materials switch at (a), (b), or (c). In fact, only two, VO₂ and Ti₂O₃, have transition temperatures (T_t) that fall within the entire range from (a) to (c). The transition in Ti₂O₃ is not very sharp, occurring between ~145°C and ~225°C. The transition in VO₂ is very sharp and large as indicated in Figure 1 and also in Figure 2, which shows the infrared transmittance switching of a thin film of VO₂ on Ge deposited by reactive sputtering at Honeywell Systems and Research Center. The low temperature transmittance is limited by reflectance loss, especially at the Ge

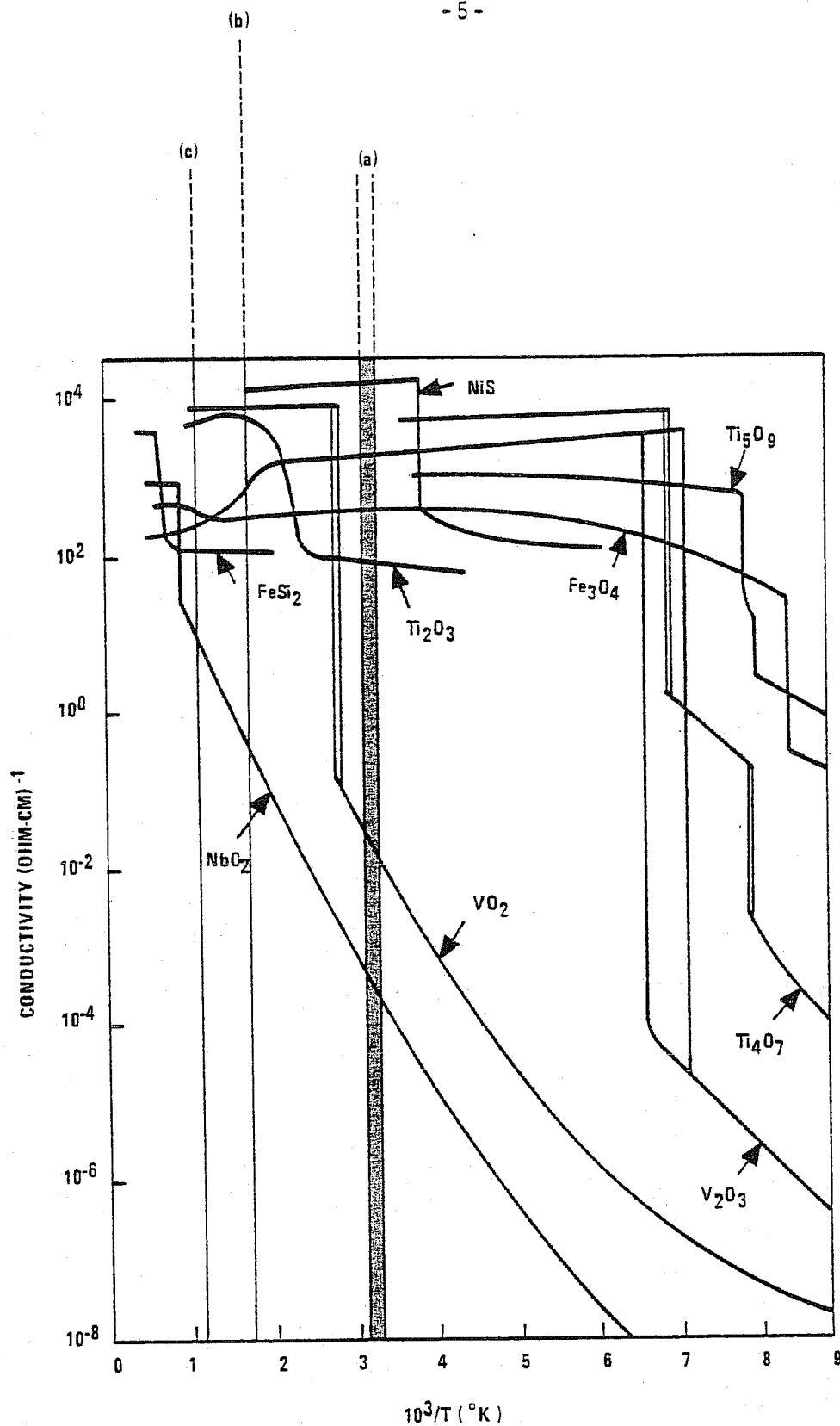


Figure 1. Electrical Conductivity as a Function of Reciprocal Temperature for Several Transition Metal Compounds (Ref. 5). (a, b and c) refer to Temperatures of Interest for Solar Energy Applications.

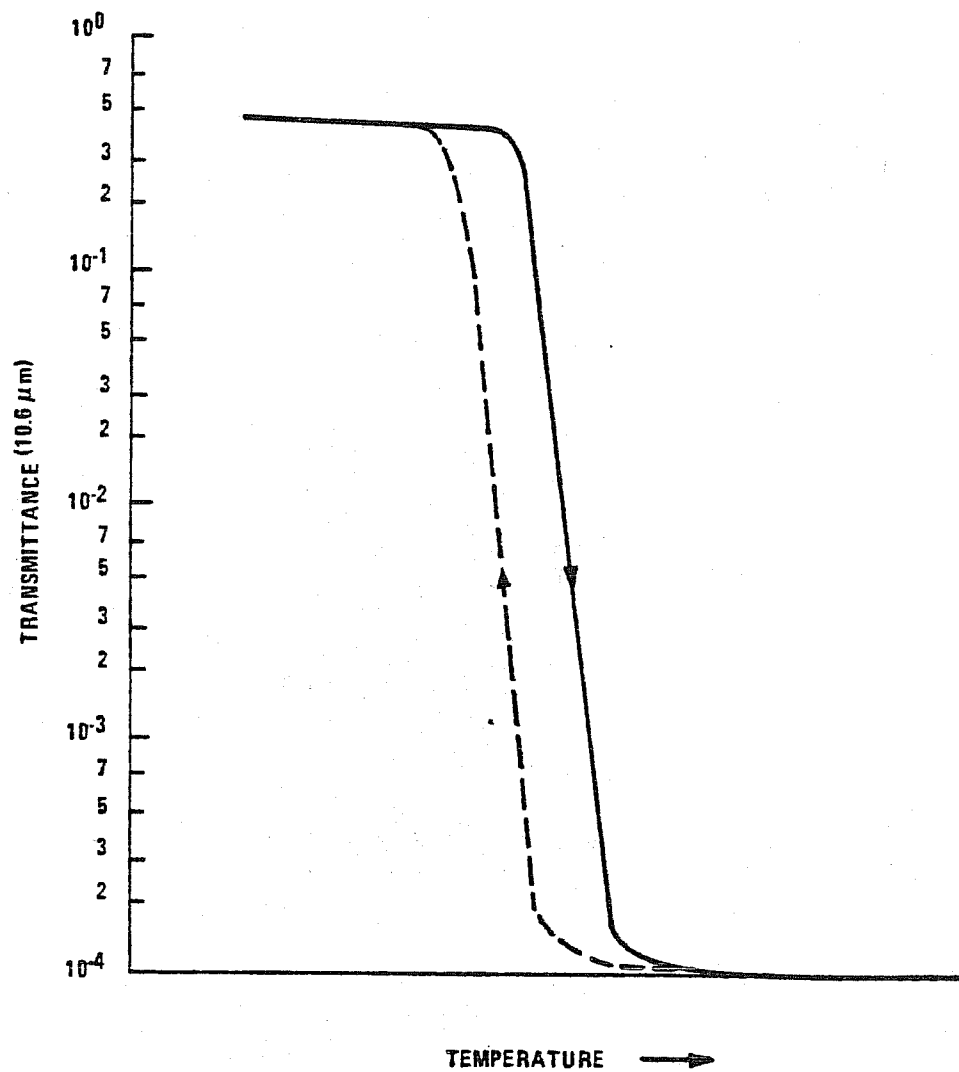


Figure 2. Switching Characteristic of VO_2 at $10.6 \mu\text{m}$ Showing the Hysteresis Effect

second surface. The VO_2 has basic problems related to its building glazings applicability: (1) Its T_t is too high (68°C), and (2) Its visible transmittance is very low (approximately 20-percent reflectance and high absorptance). The spectral switching characteristics of VO_2 , as measured at Honeywell are shown in Figure 3. Visible and near IR spectral switching characteristics as measured by other investigators are shown in Figure 4 (Ref. 11), Figure 5 (Ref. 12) and Figure 6 (Ref. 13). Note that the abscissa is scaled to give equal solar energy per unit length. Statements made in Ref. 11, and comparison of their results with others, cast some doubt on the stated film thickness. In the next subsection we will discuss the possibilities for correcting the VO_2 problems through doping. Nearly all doping experiments have involved VO_2 , probably because of the large conductivity ratio (σ/σ_0). Doping always reduces σ/σ_0 and the other materials of interest generally have small ratios ($<10^2$) in their stoichiometric form so they are not good doping candidates. An exception would be Ti_4O_7 which has a large σ/σ_0 , but at a very low temperature. The literature search did not find any references to alloying a high T_t material with a low T_t material to obtain a material with an intermediate T_t . In fact, there was only one case where doping of more than a few atomic percent could be accomplished and the resulting material still underwent a transition. In that case a non-switching material (TiO_2) was alloyed with VO_2 .

Undoped TC materials properties are shown in Table 1. Note that, as in Figure 1, many materials are included whose T_t 's fall outside of the range of interest. These materials came up in the course of the study and are included for the sake of completeness. σ refers to the electrical conductivity at $T > T_t$ and σ_0 to that at $T < T_t$. Thus, σ/σ_0 is the ratio of the conductivity switching at T_t . Table 1 contains a column showing whether or not a transition is first order. Here, a first order transition means that there is a change in the energy band because of a lattice constant change; i.e., a crystal structure change. Such a change results in a sharp transition that exhibits hysteresis and has a measurable latent heat of transition.

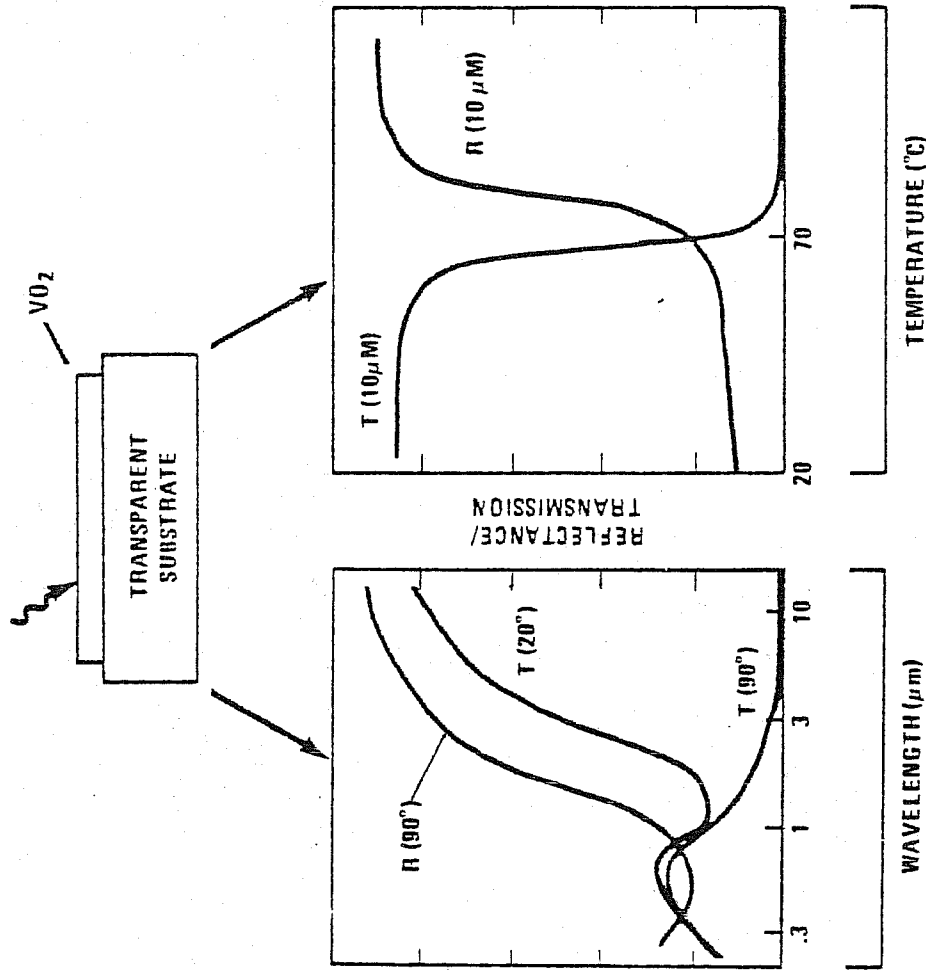


Figure 3. Spectral Switching Characteristics of VO_2

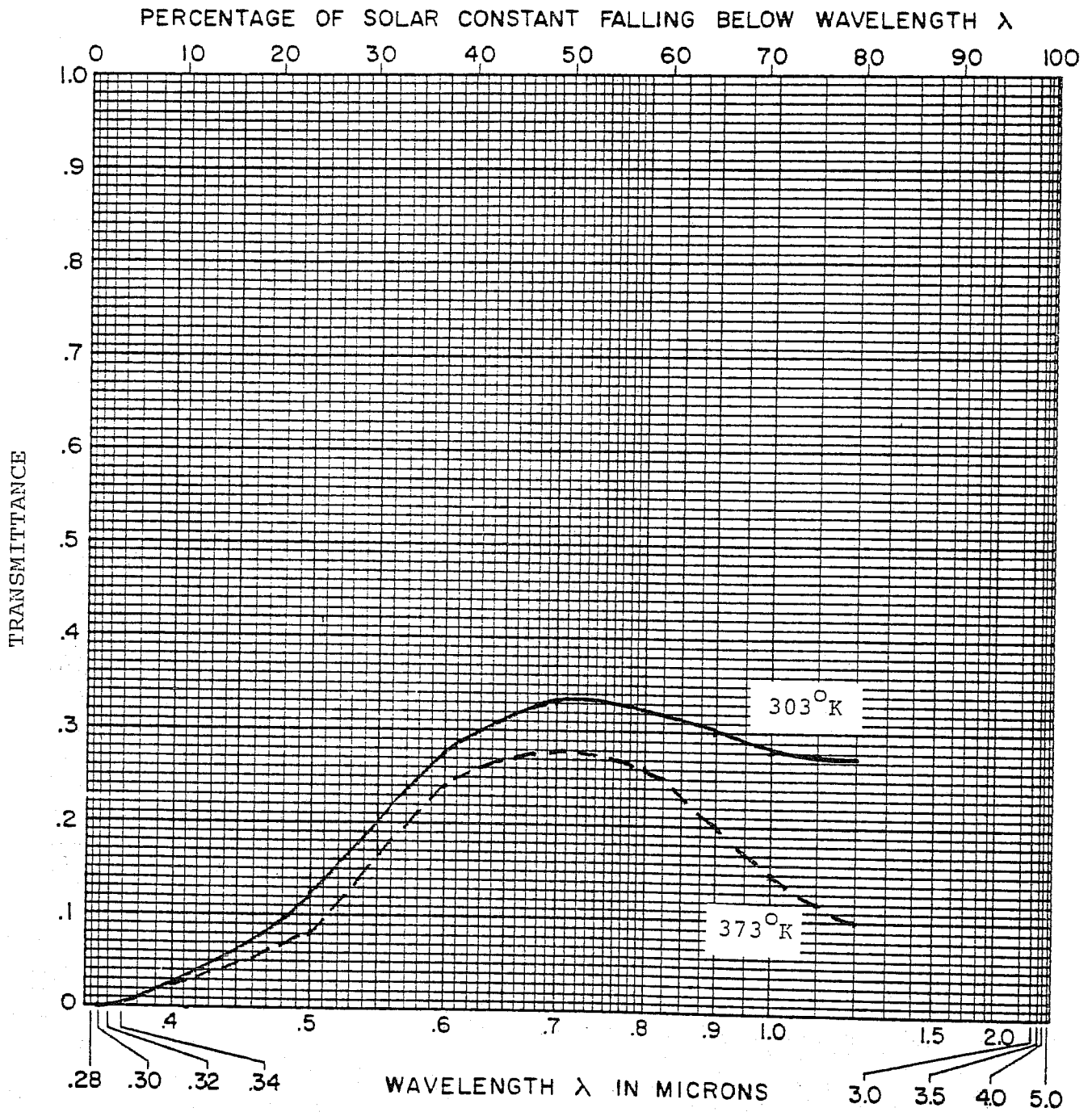


Figure 4. Spectral Transmittance of a 50nm Film of VO₂ above and below T_t (Ref. 11)

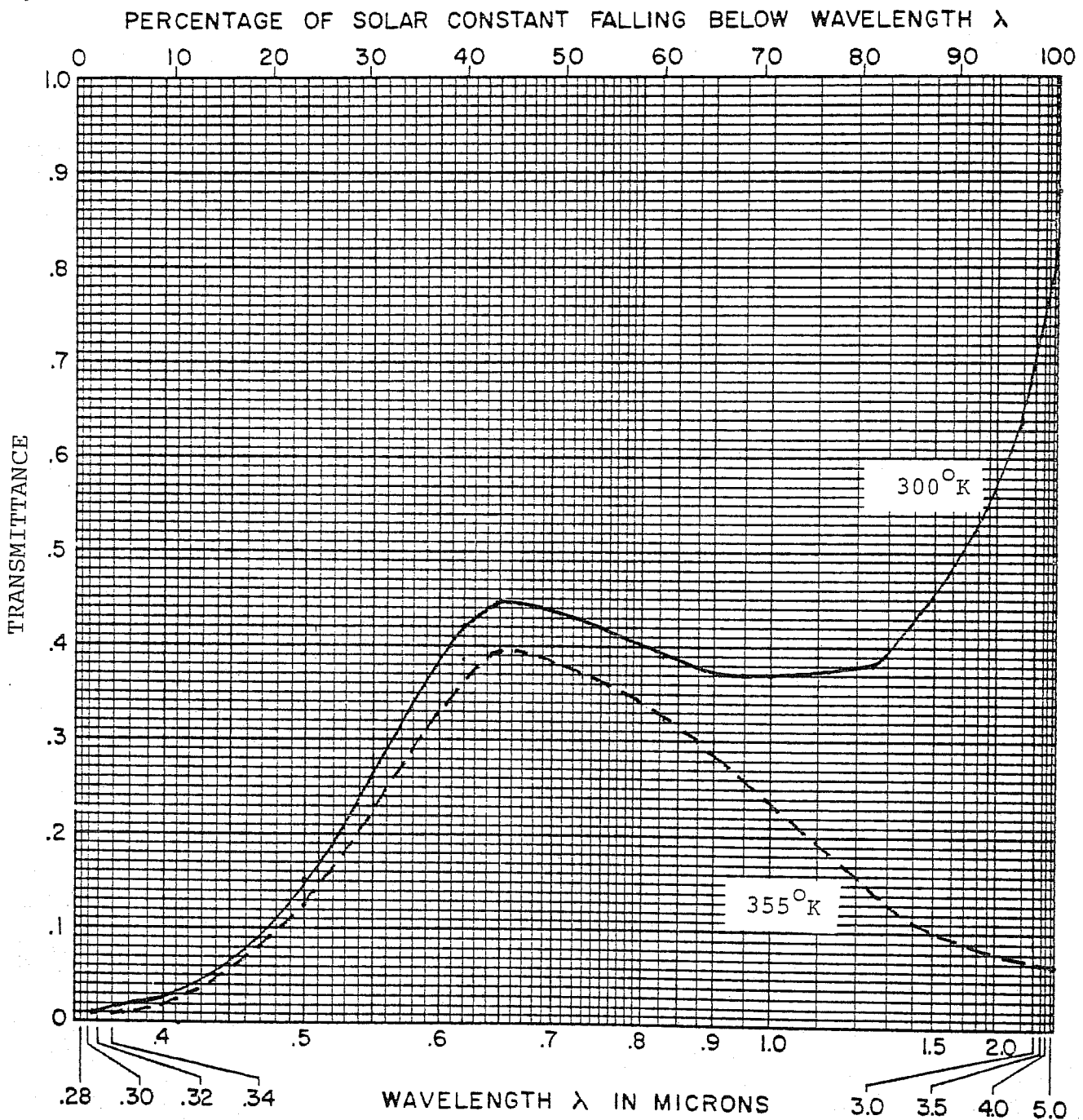


Figure 5. Spectral Transmittance of a 100nm Film of VO_2 above and below T_t (Ref. 12)

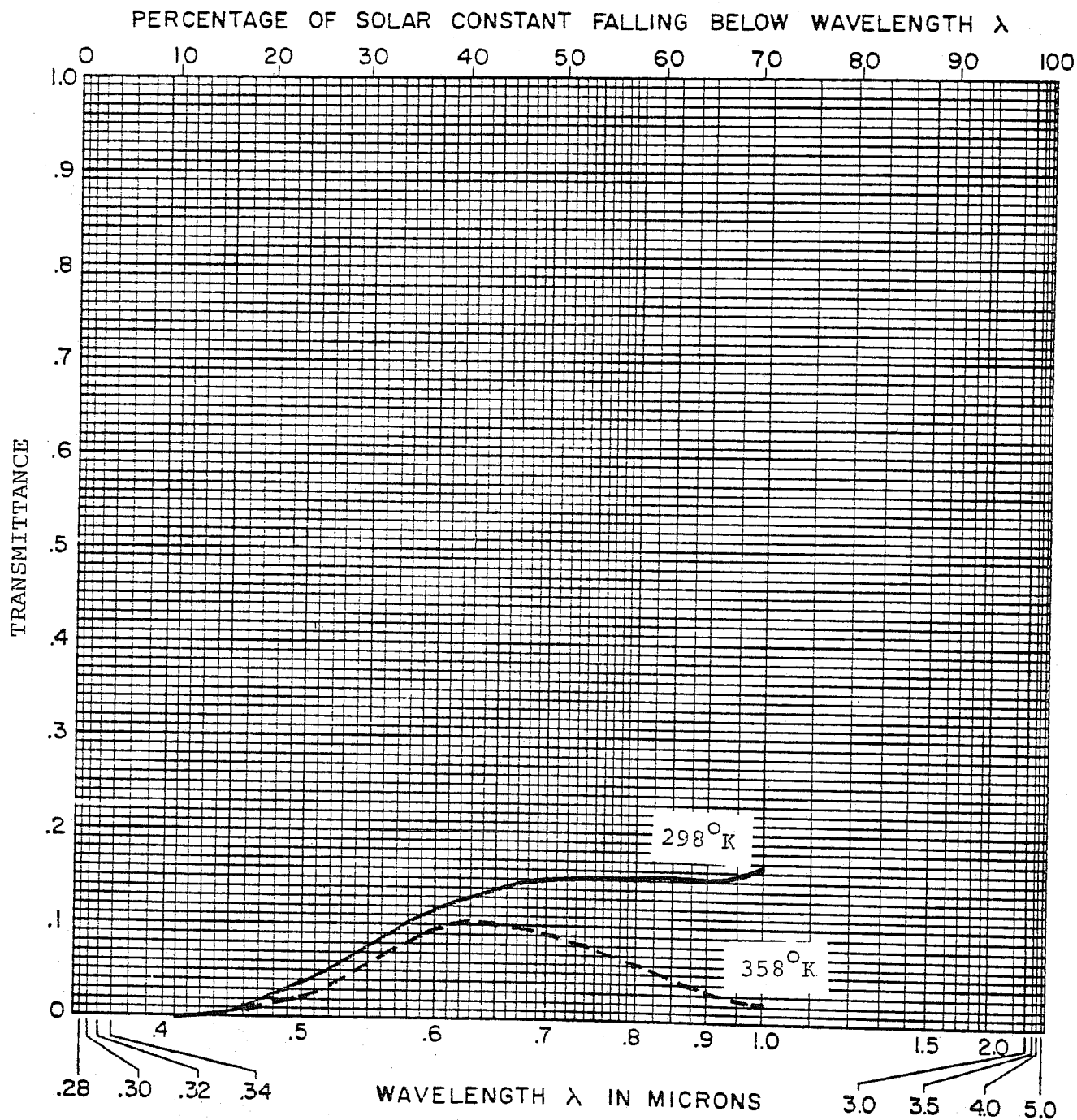


Figure 6. Spectral Transmittance of a 150nm Film of VO_2 above and below T_t (Ref. 13)

TABLE 1. TRANSITION PROPERTIES OF STOICHIOMETRIC THERMOCHROMIC MATERIALS (Cont...)

FORMULA	COLOR	SYMMETRY	MELTING POINT	RESISTIVITY (Ω - cm)	TRANSITION TEMP.	TRANSMITTANCE	REFLECTANCE	α/α_0 at T_t	1st ORDER TRANSITION	INDEX OF REFRACTION
V_6O_{13}		Monocl. (6)	981°K (21)	2.5(-6)- Ω -cm@100K 3(-5)- Ω -cm@156K 2(-4)- Ω @157K 10 ³ @300K (23)	156°K (23) Heat. 151°K Cool. 147°K (24) 173°K (25)					
Titanium Sesquioxide Ti_2O_3		Rhombohedral @ 198K (38)		0.2@300K (35)	450°K (35) 450-700 (39) 660°K (38)			10 (35), 40 (40), 40 (38)	no (19)	
Ti_3O_5		Monocl. (41) Pseudorutile @ $T < T_t$ Monocl. @ $T > T_t$ (22)		3.2x10 ⁻² @460°K 3.20-cm @ 250°K (41)	460°K (22,42,43)					
Ti_4O_7		Triclinic (41)		20-cm@ $T > T_t$ 10 ³ @ $T < T_t$ 5x10 ⁻⁴ $T > T_t$ 0.5@ $T < T_t$ (41)	149±2°K and 125°K (41) Heat. 149°K Cool. 125°K (22)			10 ³ (41)	yes yes (22)	
Ti_5O_9		Triclinic (41)		3x10 ⁻² @ $T > T_t$ 0.22@ $T < T_t$ 4x10 ⁻³ @ $T > T_t$ 3x10 ⁻² @ $T < T_t$ (41)	130°K & 136°K (41) Heat. 130°K Cool. 125°K (22)			~8 (41)	yes yes (22)	
Ti_6O_{11}		Triclinic (41)		.350-cm@ $T > T_t$ 6.30-cm@ $T < T_t$ (41)	130°K (22,41)			20 (41)	yes (22)	
Niobium Dioxide NbO_2				10 ⁴ Ω -cm@300K 16.60-cm@ $T > T_t$ (44)	1070°K (44)			10 (44)		
Nickel Monosulfide NiS		Rhombohedral < 620K Hexagonal @ $T > 620K$			260°K (45)		Spectra (0.21- 100nm) (45)	2-10 (45), 40 (46), 500 (47)		
Ferrosoferric Oxide (Magnetite) Fe_3O_4		Cubic@ $T > T_t$ Orthorh. @ $T < T_t$ (48,49)		10 ⁻² Ω -cm@119K+ 10 ⁻⁴ Ω -cm@ $T < T_t$ (48)	119°K (48)			10 ² (48) ~70 (22)		
Manganese Dioxide MnO_2				1.1x10 ⁻¹ @300°K 2.6x10 ⁻² @4.2°K	94°K (50)			~10 (50)		

TABLE 1. TRANSITION PROPERTIES OF STOICHIOMETRIC THERMOCHROMIC MATERIALS (Cont....)

	FORMULA	COLOR	SYMMETRY	MELTING POINT	RESISTIVITY (Ω -cm)	TRANSITION TEMP.	TRANSMITTANCE	REFLECTANCE	σ/σ_0 at T_t	1st ORDER TRANSITION	INDEX OF REFR. (n)
Europous Oxide	EuO				10^{11} at T_t 10^{-2} at $T < T_t$ (51)	50-60°K (51)			10^{13} (51)		
Silver Sulfide	Ag_2S	black	Monoc. at $T < T_t$ Cubic at $T > T_t$ (52)		.001-0.30 at $T > T_t$ 1-30 at $T < T_t$ (53)	450°K (53)			10^3-10^4 (52) $5 \times 10^2-10^3$ (53)	yes (52)	$n_D 0.11 \mu\text{m}$ (52)

This study revealed a shortcoming in most TC materials testing conducted to date with respect to their use in controlling solar energy transmittance and reflectance. Most of the work on these materials has been directed at using them to switch electrical signals. Consequently, there is only limited optical data available. Only VO_2 and V_2O_3 have undergone extensive optical testing.

Optical testing on VO_2 has yielded consistent results in the mid- and long-wave IR ($\lambda > 2 \mu\text{m}$). However, in the near IR and visible spectral regions there is considerable disagreement concerning transmittance both above and below T_t . Several investigators found a relatively small decrease in near IR and visible reflectance as the temperature rises above T_t (see eg. Refs. 15 and 18). Nyberg and Buhrman (Ref. 54) found that VO_2 reactively evaporated onto substrates hotter than 550°C are more transparent in the visible than 'ordinary' VO_2 and that as these films switch to the metallic state ($T > T_t$), the 600-800nm transmittance increases sevenfold. Their results lead us to believe that varying deposition conditions are the probable reason that there is disagreement. In fact, Smith and Hughes (Ref. 11) show two different transmittance results for samples deposited under different oxygen partial pressures. Clearly, there is a need to learn more about the visible and near IR optical properties of VO_2 .

DOPED THERMOCHROMIC MATERIALS

Many investigators have studied the effects of doping TC materials, some to tailor the transition to a specific application but mostly as an aid to understanding the physics of the transition. Again, most of the work has been on the vanadium oxides and because VO_2 is the only one that is close to being useful for solar energy applications, this study concentrated on dopants for that compound. In Table 2 we have shown the transition temperature as a function of composition for the compounds $\text{V}_{1-x}\text{M}_x\text{O}_2$, where M is the dopant material. Note that this data (dT_t/dx) is generally applicable only for x

TABLE 2. RATE OF CHANGE OF THE TRANSITION TEMPERATURE (T_t) NEAR T_t AS A FUNCTION OF COMPOSITION FOR THE SUBSTITUTIONAL COMPOUNDS $V_{1-x}M_xO_2$.

M	$dT_t/dx (^{\circ}K/at \% M)$	x for $T_t=310^{\circ}K$	σ/σ_0 at T_t	References
Ti	-0.5 to -0.7	45 mole % TiO_2 55 mole % VO_2	10	55,56,57
Re	~ -4			
Ir	~ -4			
Os	-7			
Ru	-10			
Nb	~ -8	0.04	<10	56,57,58,59
Ta	-5 to -10			
Mo	~ -12	0.025	100+	22,57
W	-21	~ 0.014	~ 100	60,61
		~ 0.012	~ 300	62
	~ -28	~ 0.010		63
Ge	+5			
Cr	$\sim +3$			22,56,64
Fe	+3			56
Ga	+6.5			
Al	+9			56

being small; that is, near the transition temperature. One must also be aware that even though increasing values of x lead to increasing T_t 's, they also lead to decreasing conductivity ratios (σ/σ_0). It should be pointed out that in the case of Ti, alloying might be a better term than doping.

There are two metals, Mo and W, that can be substituted in $V_{1-x}M_xO_2$ with results that appear to be useful for building glazing applications (see Table 2). Small amounts of dopant move the transition temperature to useful ranges and their electrical conductivities still undergo nonlinear transitions of the order of 100 or more. IR reflectances are expected to remain high at $T > T_t$ because the conductivities are approximately the same as for VO_2 (Ref. 62). Values for x that would shift T_t to 310°K (99°F) were determined. That temperature is in the useful range for building energy applications. These dopants could be used to move the transition temperature somewhat lower eg., it appears that approximately 1.7 atomic percent W ($x=0.017$) will move the transition temperature to approximately 70°F (Ref. 60). There were no optical data (transmittance and reflectance) available for $V_{1-x}W_xO_2$. Greenberg (Ref. 65) has measured 0.8 to 2.2 μm transmittance for a 180nm film of $VO_{0.982}Mo_{0.018}O_2$. At that doping level the transition temperature would be approximately 320°K (117°F). Greenberg also measured 0.8 to 2.2 μm transmittance of a 150nm SnO_2 -doped VO_2 film (unreduced CVD VO_x grown on a SnO_2 primed glass substrate) (Ref. 65). The data for these two materials were replotted and are shown in Figure 7. Note that the near IR transmittances for these doped films are higher than for undoped VO_2 films of the same thickness as shown in Figure 6. However, the unswitched-to-switched transmittance ratios are smaller as would be expected from conductivity data. Although these pieces of incomplete data do not reveal much optical information, they do indicate that doping of VO_2 can increase its transmittance in the near IR, and possibly in the visible, and that by extending the switching to shorter wavelengths, the solar energy switching might be increased.

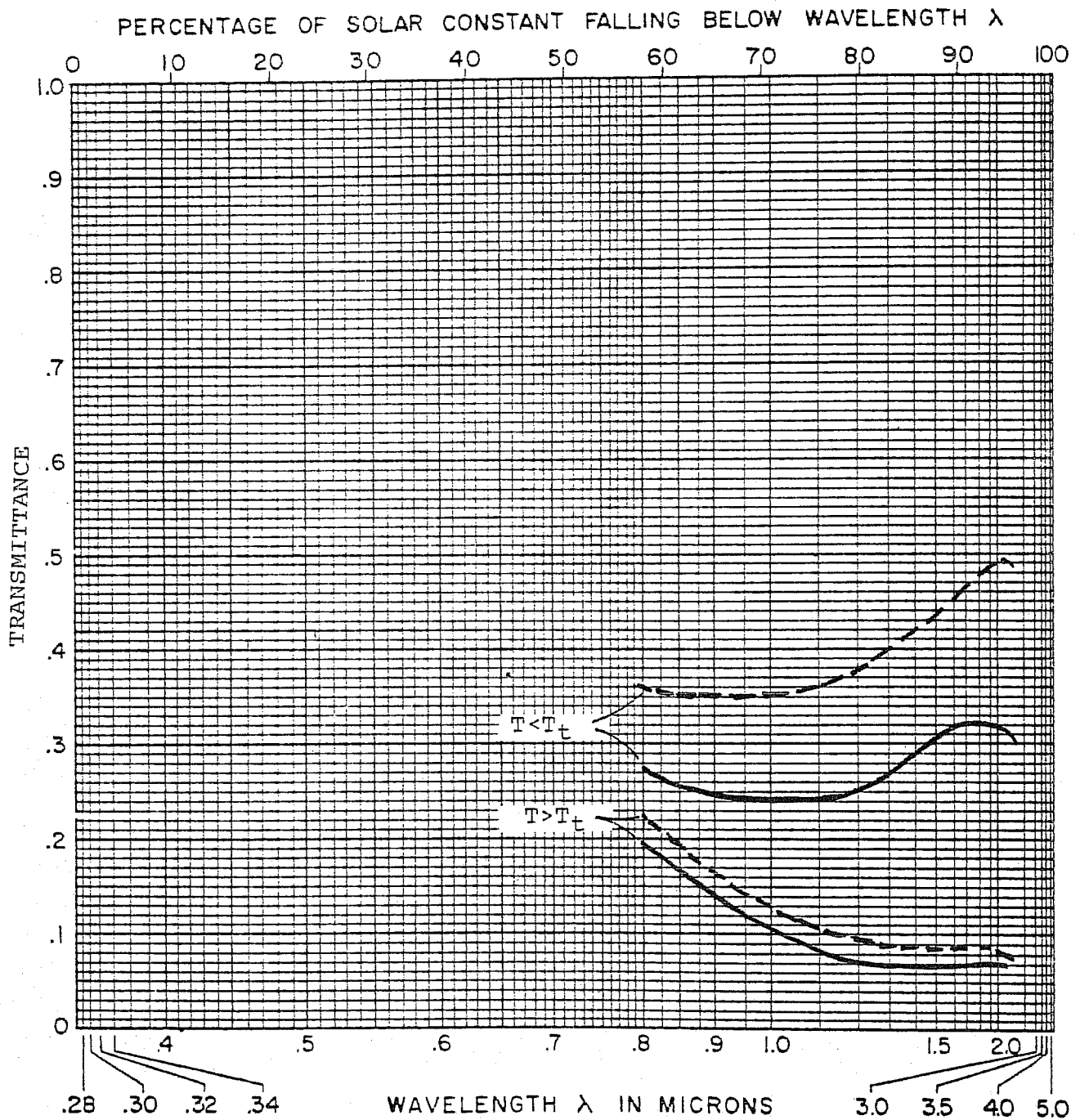


Figure 7. Spectral Transmittances of $V_{0.982}Mo_{0.018}O_2$ (solid lines) and a SnO_2 -Doped VO_2 (dashed lines) above and below their transition temperatures (Ref. 65)

Futaki and Aoki (Ref. 66) studied the transition temperature for various ternary compound Critical Temperature Resistors. Powders of V, R and P were mixed, reduced and pressed into beads ($V=V_2O_5$; $R=Fe_2O_3$, CoO , NiO , GeO_2 , TiO_2 , MoO_3 , Nb_2O_5 , WO_3 , or Ta_2O_5 ; $P=P_2O_5$). The transition temperature and the conductivity ratios at T_t for several of these ternary systems are shown in Table 3. The oxygen content is not shown. Several of the transition temperatures shown for specific compositions of these compounds are applicable for solar energy control via building glazings. However, even though their approximate change in conductivity at T_t is known, their absolute conductivities and their optical characteristics were not given.

Some work has also been directed at doping VO_2 by replacing some of the oxygen with fluorine, $VO_{2-x}F_x$ (Refs. 67,68). The transition temperature is shown in Ref. 67 to be linearly related to x , with the dT_t/dx being approximately $-26^\circ K/\text{atomic percent F}$ (Ref. 67 shows a T_t of $310^\circ K$ and a $\sigma/\sigma_0 > 300$). Thus, transition temperatures applicable to solar energy control through building glazings is achievable at the low fluorine levels of a little more than one atomic percent. From Refs. 67 and 68, such a material must be metallic ($\sim 10^{-2}$ to $10^{-3} \Omega\text{-cm}$) above the transition temperature and semiconducting (~ 0.2 to $5 \Omega\text{-cm}$) below T_t . Even though there was no optical data, this material is expected to transmit at $T < T_t$. It is also expected to reflect well in the IR at $T > T_t$, but the visible and near IR responses are unknown. An interesting possibility is that this material might transmit to shorter wavelengths as most fluorides do.

Sakata (Ref. 69) has doped NbO_2 by the substitution of Ti in $Nb_xTi_{1-x}O_2$. A linear relationship of $dT_t/dx \sim -20^\circ K/\text{atomic percent Ti}$ was found for $0.9 < x < 1.0$. However, stoichiometric NbO_2 has a $\sigma/\sigma_0 \sim 10$ at T_t and all the other materials exhibit decreasing σ/σ_0 with increasing doping level. Consequently, we think that doping NbO_2 to drop its transition temperature into the $600^\circ C$ range is not a worthwhile endeavor.

TABLE 3. TRANSITION TEMPERATURES AND CONDUCTIVITY SHIFTS
FOR TERNARY COMPOUNDS (Oxygen not shown) (Ref. 66).

	$T_t (^{\circ}\text{K})$	σ/σ_0 at T_t
$\text{V}_7\text{Fe}_3\text{P}_{2.5}$	328	100+
$\text{V}_{8.9}\text{Mo}_{0.1}\text{P}_{1.0}$	323	~ 15
$\text{V}_{8.7}\text{Mo}_{0.3}\text{P}_{1.0}$	299	10+
$\text{V}_{8.5}\text{Mo}_{0.5}\text{P}_{1.0}$	283	$\sim 5-6$
$\text{V}_{8.7}\text{Nb}_{0.3}\text{P}_{1.0}$	323	
$\text{V}_{8.9}\text{W}_{0.1}\text{P}_{1.0}$	312	~ 15
$\text{V}_5\text{Co}_3\text{P}_2$	329	~ 100
$\text{V}_8\text{Ge}_1\text{P}_1$	353	~ 30
$\text{V}_{7.1}\text{Sr}_{1.8}\text{P}_{1.1}$	340	$\sim 1500-2000$
$\text{V}_{10}\text{P}_{1.1}$	338	~ 2500

OTHER EFFECTS ON T_t

In addition to doping, there are other effects that can cause shifts in the transition temperature (T_t) of thermochromic materials. Duchene, et al. (Ref. 70) found that overcoating a VO_2 film with a thin film of SiO_2 lowered its T_t , decreased its σ/σ_0 and spread the transition out over approximately 30°C . Several investigators have studied the relationship between T_t and pressure and stress, especially in V_2O_3 (Refs. 28,71,72,73). Adler, et al. (Ref. 32) point out that the pressure effect is much smaller in VO_2 than in either V_2O_3 or VO . We expect that the overcoated VO_2 is affecting T_t by its intrinsic stress or by limiting the atomic reorientation that occurs at transition. Serbinov, et al. (Ref. 17) found that VO_2 can be switched electrically and that as the temperature is increased toward T_t , the electric field required for switching decreases. This would indicate that a constantly applied low electric field could be used to reduce the transition temperature. Our experience at HSRC, as well as that of others, indicates that VO_2 does not switch electrically over large areas. Rather, the field causes formation of high conductivity filaments, which cannot be used for the solar energy applications of interest in this study.

Generally, these other effects are of interest to help us understand the Physics of the transitions. They do not appear to be useful in practice and will not be discussed further in this report.

CONCLUSIONS

A look at Figure 1 makes it clear that the only TC material useful for building glazing applications would be VO_2 that has been modified (doped) to decrease its transition temperature by approximately 30°C . That kind of modification is possible but the optical properties of doped VO_2 's might not be acceptable. For this application a large σ/σ_0 is not required. Therefore, a relatively thin film of 200nm, or less, might give useful switching and acceptable visible transmittance. There really are no TC materials that can be

used for solar collector glazing (Figure 1, line b). Ti_2O_3 is the closest but it switches by a ratio of less than 100 in its stoichiometric, single crystal, form. Also, in addition to reducing the switching effect by doping, we found no data on dopants that increase T_t in Ti_2O_3 . V_3O_5 has been reported (Refs. 18 and 36) to have $T_t \sim 420^\circ K$. However, it only switches by a ratio of about 10 to 20 and we also found no data on doping V_3O_5 to move T_t to higher temperatures. NbO_2 is the only TC material that could be used for a solar absorber application (Figure 1, line c). Its T_t is too high by approximately $200^\circ C$ but that can be corrected through doping (Ref. 69). However, as pointed out earlier, the conductivity ratio (σ/σ_0) in NbO_2 is only approximately 10, and doping would reduce that to something that is not useful. Therefore, the only applicable TC material is doped VO_2 , for use in conjunction with building glazing.

Doped VO_2

There are several dopants that can be added to VO_2 to decrease its transition temperature (T_t) down into the range of $300-310^\circ K$, where it would be useful for controlling solar energy flow through building glazing. All dopants reduce the conductivity ratio (σ/σ_0) with increasing doping level. Therefore, the most promising candidate dopants are those with large dT_t/dx (T_t change per atomic percent dopant) so that small quantities of dopants are required. From Table 2, W looks best, then Mo and possibly Ru but there is essentially no data on Ru.

Approximately 1 to 1 1/2 atomic percent of W in VO_2 ($V_{0.99}W_{0.01}O_2$ to $V_{0.985}W_{0.015}O_2$) will switch in the temperature range of 26 to $46^\circ C$ with a conductivity ratio of approximately 100 to 500. Such a material could be deposited on glass by vacuum deposition (evaporation or sputtering) either by using doped source material or by co-depositing from two sources. The technology needed for depositing this material is available.

There are several issues associated with the application of doped VO_2 coatings for controlling solar fluence through windows:

- o Can doped VO_2 be fabricated to give acceptable visible transmittance in both states ($T < T_t$ and $T > T_t$)?
- o Will the doped VO_2 have a pleasing color, both in transmittance and from the exterior (reflectance)?
- o Can the spectral response of the doped VO_2 be tailored to achieve more switching at shorter wavelength?
- o The total U.S. production of V is approximately 2000 tons per year, mainly used for alloying steels. Would there be a sufficient quantity available at reasonable cost for a major new application?

These are questions that must be answered before decisions about applicability of doped VO_2 can be made.

ELECTROCHROMIC MATERIALS

INTRODUCTION

Electrochromic materials or systems change their color reversibly in response to an applied electric potential. They are usually divided into inorganic ion insertion (transition metal oxides) or organic ion insertion materials and reversible electrodeposition systems. Nearly all the reported work on electrochromic materials has been directed at developing display devices and therefore, much of the literature does not provide some of the information necessary to assess solar energy applicability. Also, most of the ion insertion materials are used in electrochemical cells wherein the electrolyte material is a liquid. Although that does not preclude their use on large surfaces, such a system would probably be impractical. Some solid electrolyte systems have been tested and it appears that they are effective (Refs. 74,75).

INORGANIC ION INSERTION

Tungsten trioxide (WO_3) is the most widely studied of this class of EC materials. A cell using a sputter deposited thin film of WO_3 , a solid electrolyte (RbAg_4I_5) and Indium Tin Oxide (ITO) as the transparent electrode exhibited good switching characteristics in the solar spectrum (Ref. 75). In Figure 8 we have plotted the 0.4 to 2.5 μm colored state transmittance of this WO_3 cell relative to the 'clear' state transmittance. Note again that the abscissa is scaled to give equal solar energy per unit length. The integrated solar transmittance is 0.47 for 0.4 to 2.5 μm . Therefore, this cell shuts off 53 percent of the radiation in that band, which contains approximately 84 percent of the total solar energy and even more that of the solar energy that would be transmitted through glazing. Thus, this material could be used to reduce the influx by approximately one-half. The energy requirement for this system is approximately 10 mJ/cm^2 for each complete cycle (clear to colored to clear) and the potential is approximately 2.75V. Goldner, et. al. (Ref. 76) were interested in solar energy applications and have measured the spectral reflectance of bleached and colored polycrystalline WO_3 deposited by rf sputtering on ITO substrates. Their data is replotted in Figure 9 from which the 0.5 to 2.5 μm integrated solar reflectance can be seen to change between 0.13 and 0.27. Thus, they show an increase by a factor of two in the integrated reflectance for approximately 73 percent of the total solar spectrum. Of course, that would decrease if the 0.4 to 0.5 μm reflectances are similar to those between 0.5 to 0.6 μm (lower in the colored state than in the 'clear' state).

Molybdenum trioxide (MoO_3) is another material that has been studied extensively. In the example presented here an aqueous electrolyte was used (Ref. 77). In Figure 10 we again plot spectral transmittance in the colored state relative to the 'clear' state. The 0.4 to 2.5 μm integrated transmittance is 0.34. Thus, this system can be used to exclude 66 percent of the 0.4 to 2.5 μm radiation. Depending on the configuration, this system requires a potential of 2.5V or less.

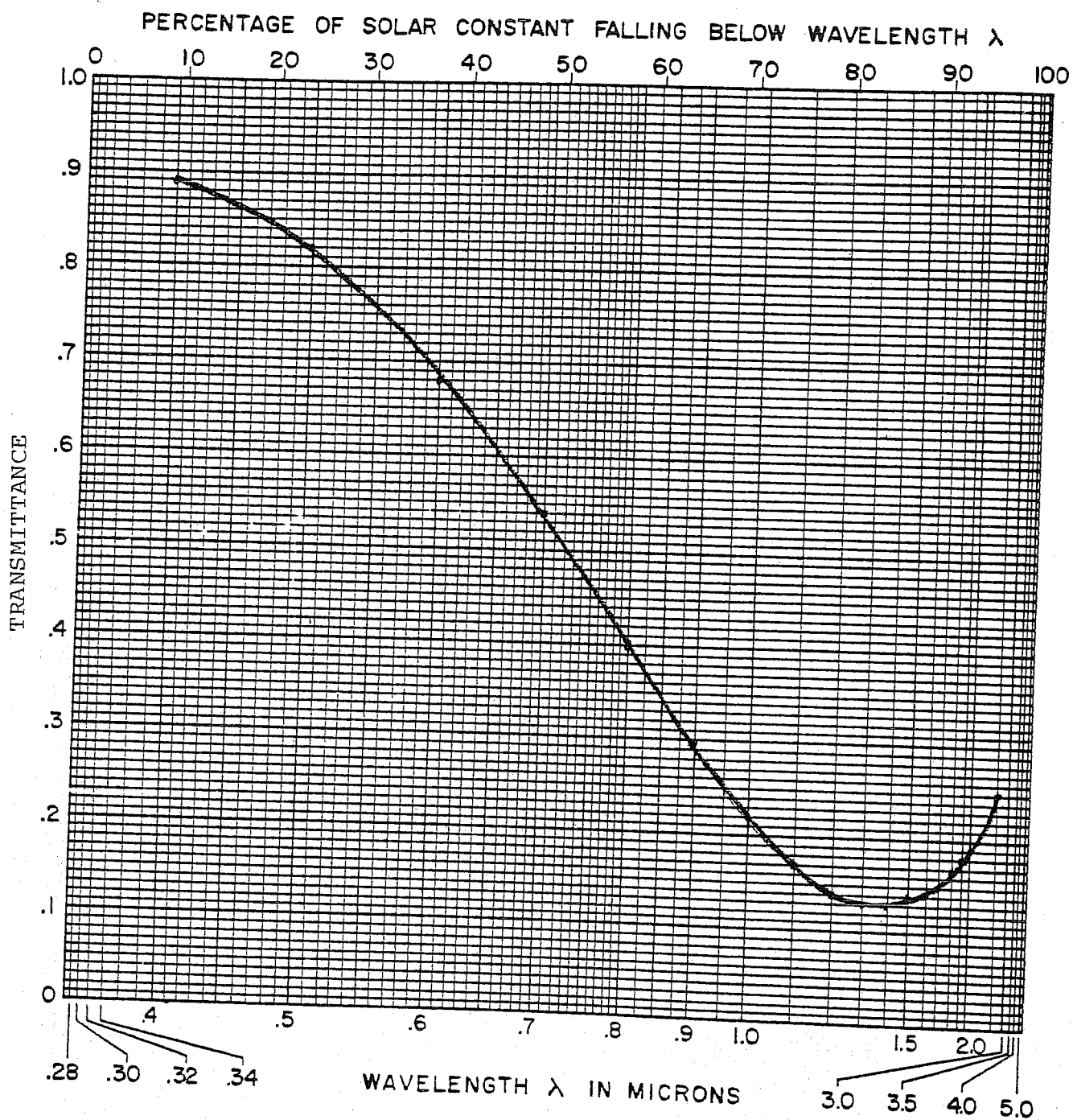


Figure 8. Colored State Transmittance (T) of WO_3 Relative to the "Clear" State Transmittance (T_0). $T/T_0 \sim 0.47$ (0.4-2.5 μm)

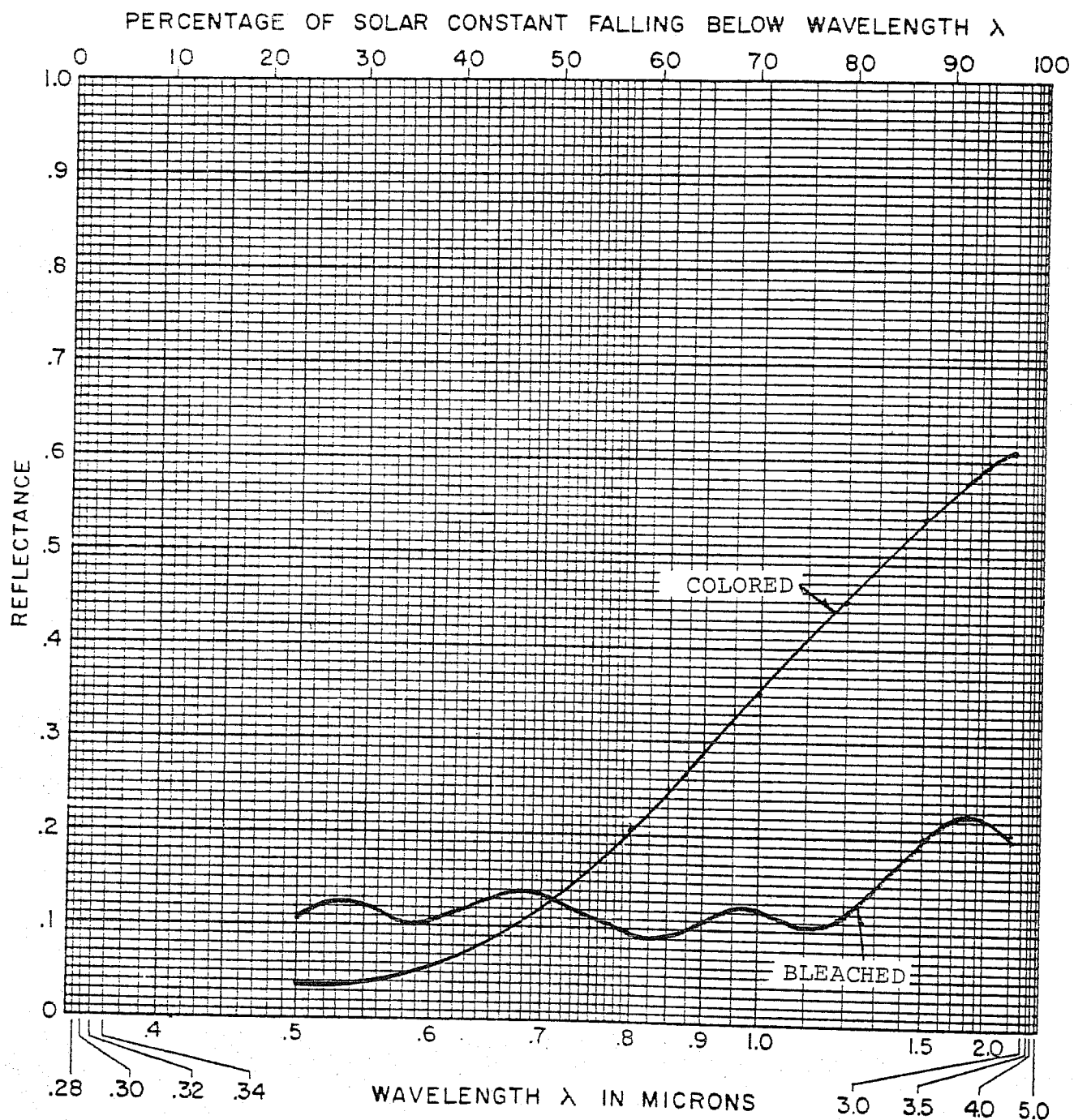


Figure 9. Solar Reflectance (0.5-2.5 μ m) of WO_3 on ITO in Colored State ($R_s \sim 0.27$) and Bleached State ($R_s \sim 0.13$) (Ref. 76).

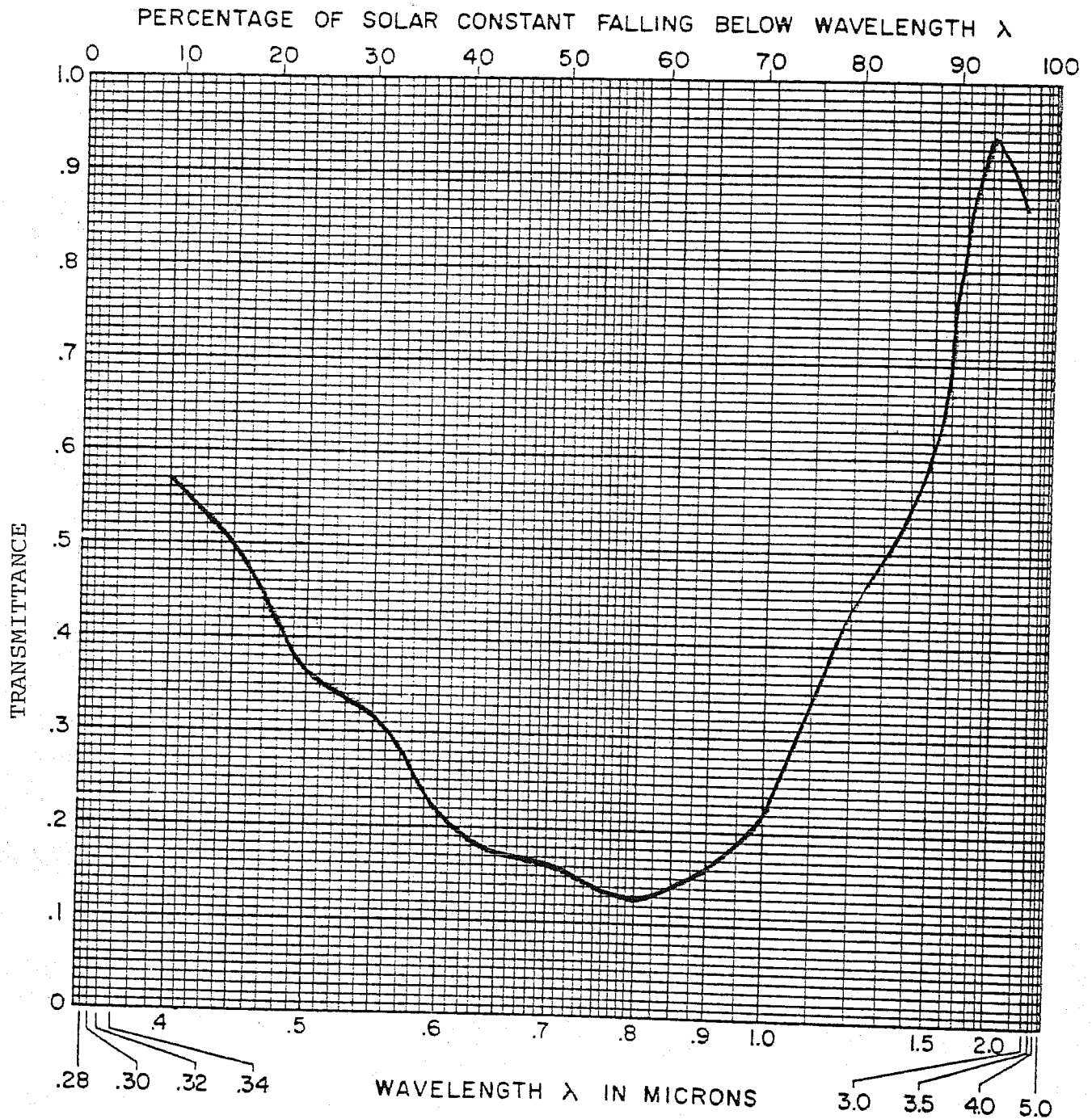


Figure 10. Colored State Transmittance (T) of MoO_3 Relative to the "Clear" State Transmittance (T_0). $T/T_0 \approx 0.34$ (0.4-2.5 μm)

The data that was found on inorganic ion insertion EC materials is shown in Table 4. The column headed T/T_0 refers to the solar transmittance of the 'colored' relative to the 'clear' states. As discussed above, WO_3 is the most promising EC material, and for solar glazing or collector applications it should be used in conjunction with a thin film solid electrolyte.

Vezzoli (Ref. 87) discusses an insulator-to-metal field-induced phase transition in niobium dioxide (NbO_2) when in the presence of a sufficient charge concentration. Earlier, this electric field induced transition was also investigated by Shin, et al. (Ref. 88). Honeywell Systems and Research Center has worked on the task of depositing NbO_2 thin films that will switch upon application of an electric field. HSRC has had two government contracts and has worked the problem on IR and D for three years. NbO_2 has to be deposited with good stoichiometry and crystallinity, but more than that, the crystallites must be properly aligned. HSRC has now deposited NbO_2 that switches electrically. However, at this stage of development, the devices draw too much current and considerably more development will be necessary before electric field switched thin film NbO_2 will be a reality.

ORGANIC ION INSERTION

The organic ion insertion electrochromic materials that have been studied most extensively are the viologens and specifically, heptyl viologen dibromide (HVDB). HVDB has high electrochromic efficiency, or sensitivity, which is excellent for display applications because its two peaks are at 513.5 and 544nm. However, for solar energy applications this is not desirable because there is essentially no switching except at the center of the visible spectrum. Therefore, there would be a large change in the visible region (appearance) without a large integrated solar effect. This could be useful for daylight control. This rather narrow-band effect appears to be more typical of the organic ion insertion materials than of the inorganic materials. Table 5 contains data on several organic EC materials that exhibit significant

TABLE 4. INORGANIC ION INSERTION ELECTROCHROMIC MATERIALS DATA

MATERIAL	ELECTROLYTE	ELECTRICAL REQMENTS		T/T ₀	COMMENTS	REF.
		POTENTIAL	ENERGY			
WO ₃	Sol. RbAg ₄ I ₅	2.75V	10mJ/cm ² (each cycle)	~0.5		75
MoO ₃	H ₂ SO ₄ in H ₂ O & glycerol	2.5V		~ 0.35-0.45		77
Re ₂ O ₇	H ₂ SO ₄	Small (1.5V?)		≤ 0.55	Hygroscopic	78
80% V ₂ O ₅ / 20% P ₂ O ₅	H ₂ SO ₄			~ 0.67	Lt. brown in "clear" state	78
WO ₃	Acidic gel			~ 0.55		79
SrTiO ₃ ·Ni, Mo,Al	Solid Dopants			~0.5	"Blue" single crystal, 15mm, 3mmx ≤1mm	80
IrO ₂	H ₂ SO ₄	1V	20mJ/cm ² (each cycle)	~0.5 (reflectance) (@633nm)	Anodic-Oxide	81,82
IrO ₂	H ₂ SO ₄	1V	30mJ/cm ² (each cyc)	~0.35 (@633nm) (reflec.)	Sputtered oxide	81
RhO ₂ NiO ₂ CoO ₂					Less effective than IrO ₂ or WO ₃	81

TABLE 5. ORGANIC ION INSERTION ELECTROCHROMIC MATERIALS DATA

MATERIAL	ELECTROLYTE	ELECT. REQMTS.		I/I ₀	COMMENTS	REF
		POTENTIAL	ENERGY			
Polytungsten Anion				~0.4 (0.4-1.3 μm)		79
Heptyl Viologen Dibromide		1-2V	4mJ/cm ² (1 cycle)	~0.65 (0.4-1.3 μm)		79,83
PVBCT*	(CH ₃ N) ₄ CIO ₄	0.8V	5.7mJ/cm ² (1 cycle)	~0.9	All change between 0.35-0.65μm	84
Lutetium Di-Phthalocyanine	KCl	1.5V	4mJ/cm ² (1 cycle)		Various colors depending on applied voltage	85
Poly (N Methyl Pyrrole)	Tetraethylammonium tetrafluoroborate Et ₄ NBF ₄	~1V		~0.6 (0.45-0.85μm)	Film thickness ~0.3μm	86
Polypyrrole	Et ₄ NBF ₄	1V		~0.6 (0.45-0.85μm)	Film thickness, ~0.1μm	

*Poly (vinyl benzyl carboxy tetrathiafulvalene)

transmittance switching. There are many other organic EC materials also, but none were found with properties that have any chance for application in glazings. Also, these materials generally cannot tolerate the high temperatures of solar absorbers.

CONCLUSIONS

In their present state of development it appears that the inorganic ion insertion EC materials have the best chance for solar energy control applications. They are also the only ones that have a chance to be used in switching solar absorbers. Wet chemical electrolytes appear to be relatively undesirable for building glazings and probably not useable in solar collectors. However, there now are solid thin film electrolytes that give good results, at least with WO_3 .

The best choice at this time is WO_3 but that might be partly because it has been studied most extensively. WO_3 has the advantage that it switches most in the solar IR and maintains high visible transmittance in both states. Its integrated switched-to-unswitched transmittance is approximately 0.5, so WO_3 would give considerable control.

Some issues associated with using EC materials for solar energy control are as follows:

- o There is very little 'solar spectrum' optical data available
- o Solid electrolytes with high visible transmittance need to be developed-visible transmittance of those already developed is generally unknown (unpublished).
- o NbO_2 requires additional development to obtain good electric field switching in thin films, and then, they might not be useable where good visible transmittance is necessary.

Reversible electrodeposition systems do not appear to be adaptable to building glazing. Also, the inorganic systems that have been developed for display applications have narrow-band responses in the visible region which is not desirable for solar applications but could probably be used for daylight control. Therefore, as stated earlier, we think that the best chance for success in applying EC materials for solar energy control is to work on the inorganic materials (especially WO_3) and on solid electrolytes.

RECOMMENDATIONS

Based on this search of the literature on EC and TC materials for use in solar energy control, these are the recommendations for future development activity.

Conduct Research on Doped VO_2 --The possibilities for using doped VO_2 to control solar energy influx through building glazing should be established through performing the following tasks:

- o Deposit VO_2 doped with a range of dopant levels of a variety of dopants that will yield T_t 's in the desired temperature range. The substrates should be architectural glass.
- o Measure the solar spectral transmittances and reflectances of the deposited samples to determine which dopant(s) and dopant level(s) will provide the best solar energy control.
- o Evaluate the environmental stability of the chosen combination(s) by measuring abrasion resistance, adherence to substrate and humidity tolerance.

Conduct Optical Testing on EC Materials--Most of the research on EC materials is directed at their use in displays. To determine their usefulness for solar energy control through building glazing requires performance of the following tasks:

- o Acquire EC devices that are designed to operate in a transmission mode.
- o Fabricate EC devices that are not currently available (many devices have been fabricated for display purposes only and operate only in reflective mode; ie., they are opaque in both the 'colored' and 'clear' states).
- o Measure the solar spectral transmittance and reflectance of these candidate EC materials in both their 'colored' and 'clear' states.

Develop Solid Electrolytes for EC Devices--Building glazing comprised of EC devices with fluidic electrolytes are probably impractical. Assuming that some of these materials have desirable optical characteristics, to make these devices practical will require performance of the following tasks:

- o Investigate the range of candidate solid electrolytes for each candidate EC material, fabricating devices of the various EC material-electrolyte combinations.
- o Measure the solar spectral transmittance and reflectance of all the combinations in both the 'colored' and 'clear' states.
- o Optimize those combinations that give the best results.

Develop Switchable Thin Film NbO₂--There is good, but not irrefutable evidence, that bulk NbO₂ will switch electrically when an electric field is applied in the right direction relative to the crystal orientation. Honeywell Systems and Research Center has been working on depositing thin film NbO₂ that will switch electrically. Although there has been some success, much work is still needed to have good devices. To get to that point, the following tasks must be completed:

- o Fabricate a wide variety of thin film NbO₂ devices with variables such as: crystallite size; crystal orientation with respect to electric field; dielectric material, thickness and geometry (for insuring field rather than filamentary switching) and device size.

- o Conduct an exhaustive testing program of the fabricated devices and attempt to correlate switching characteristics with microstructure. Measure switching times to establish the presence of electric field switching.
- o Using the understanding of the process gained in the above task, fabricate larger area thin film NbO_2 EC devices for testing.

HSRC experience to date has been with NbO_2 films of $\sim 1\mu\text{m}$, or more, and they have very little visible transmittance. Thus, NbO_2 would be useable for glazing applications only if its visible transmittance is adequate in thinner films, and if the electric field switching can be realized in those thinner films.

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REFERENCES

1. Lampert, C.M., Durable Innovative Solar Optical Materials - The International Challenge. Proc. of SPIE, V. 324 Optical Coatings for Energy Efficiency and Solar Applications, 1982, pp 1-7.
2. Lampert, C.M., Solar Optical Materials for Innovative Window Design. Presented at the Window Energy Show, Las Vegas, NV., Aug. 9-11, 1982, Lawrence Berkeley Laboratory Report LBL-14694.
3. Selkowitz, S.E., et al., Advanced Optical and Thermal Technologies for Aperture Control. Presented at the Passive and Hybrid Solar Energy Update, Washington, D.C., Sept. 15-17, 1982. Lawrence Berkeley Laboratory Report LBL-15131.
4. Lampert, C.M., Electrochromic Materials and Devices for Energy-Efficient Windows. Lawrence Berkeley Laboratory Report LBL-16073, to be published in Solar Energy Materials. 1984.
5. Adler, D., Electronic Phase Transitions, DTIC Technical Report AD741459, 1972.
6. Donnay, J.D.H. (Editor), Crystal Data, Determinative Tables, 2nd Edition. American Crystallographic Association, Apr. 1, 1963. ACA Monograph No. 5.
7. Cook, O.A., High Temperature Heat Contents of V_2O_3 , V_2O_4 , and V_2O_5 . American Chem. Soc., J., V. 69, No. 2, Feb. 1947, pp 331-333.
8. Rozgonyi, G.A. and D.H. Hensler. Structural and Electrical Properties of Vanadium Dioxide Thin Films. J. of Vacuum Sci. and Technology, V. 5, No. 6, Nov./Dec. 1968. pp 194-199.
9. Paul, W., The Present Position of Theory and Experiment for VO_2 . Mat. Res. Bull, V. 5, 1970, pp 691-702.
10. Chamberland, B.L., The Hydrothermal Synthesis of $V_2O_4-xF_x$ Derivatives. Mat. Res. Bull., V. 6, 1971, pp 425-432.
11. Smith, F.A. and A.E. Hughes, The preparation and Properties of Vanadium Dioxide Films. Materials Development Division, AERE, Harwell, HL75/690 (C14). February 1975, pp 1-13. ISBN-0-70-580075-X.
12. Verleur, H.W., et al., Optical Properties of VO_2 between 0.25 and 5 eV. Phys. Rev., V. 172, No. 3, Aug. 15, 1968, pp 788-798.
13. Smith, A.W., Optical Storage in VO_2 Films. Appl. Phys. Letters V. 23, No. 8, 15 October, 1973, pp 437-438.

14. Barker, A.S., Jr. et al. Infrared Optical Properties of Vanadium Dioxide Above and Below the Transition Temperature. Phys. Rev. Letters, V. 17, No. 26, Dec. 26, 1966, pp 1286-1289.
15. Borisov, B.S., et al., Electrical and Optical Properties of VO₂ Near the Semiconductor-Semimetal Transition Point. Sov. Phys-Solid State, V. 12, No. 8, February 1971, pp 1763-1769.
16. Bongers, P.F. Anisotropy of the Electrical Conductivity of Vanadium Dioxide Single Crystals. Solid State Comm., V. 3, No. 9, Sept. 1965, pp 275-277.
17. Serbinov, I.A., et al., Phase Transition and Switching in Pyrolytic VO₂ Films. Thin Solid Films, V. 27, 1975, p 171.
18. Chadnovskii, F.A., Metal-Semiconductor Phase Transition in Vanadium Oxides and Technical Applications, Sov. Phys. Tech. Phys., V. 20, 1976, p 999.
19. Adler, D. and H. Brooks. Theory of Semiconductor-to-Metal Transitions. Phys. Rev., V. 155, No. 3, 15 March 1967, pp 826-840.
20. Okinaka, H., et al., Electrical Properties of the V₅O₉ Single Crystals. Phys. Soc. of Japan, J., V. 28, No. 3, Mar. 1970, p 803.
21. Kosuge, K., The Phase Diagram and Phase Transition of the V₂O₃-V₂O₅ System, J. of Phys. and Chem. of Solids, V. 28, No. 8, Aug. 1967, pp 1613-1621.
22. Honig, J.M. and L.L. VanZandt. The Metal-Insulator Transition in Selected Oxides. 1975 Annual Review of Materials Science, V. 5, 1975, pp 225-278.
23. Kachi, S., et al., Electrical Conductivity of Vanadium Oxides. Phys. Soc. of Japan, J., V. 18, 1963, pp 1839-1840.
24. Saeki, M., et al., Crystal Growth of V₆O₁₃. J. Cryst. Growth, V. 18, 1973, pp 101-102.
25. Kosuge, K., et al., Phase Diagram and Magnetism of V₂O₃-V₂O₅ System. J. Phys. Soc., Japan, V. 18, 1963, pp 318-319.
26. Okinaka, H., et al., Electrical Properties of V₆O₁₁ and V₇O₁₃ Single Crystals. Phys. Soc. of Japan, J., V. 29, No. 1, Jan. 1970, pp 245-246.
27. Okinaka, H., et al., Electrical Properties of the V₄O₇ Single Crystals. Phys. Soc. of Japan, J., V. 28, No. 3, Mar. 1970, pp 798-799.

28. Feinleib, I. and W. Paul. Semiconductor-to-Metal Transition in V_2O_3 . Phys. Rev., V. 155, No. 3, Mar. 15, 1967, pp 841-850.
29. Stringer, J., The Vanadium-Oxygen System-A Review, J. of Less-Common Metals, V. 8, No. 1, Jan. 1965, pp 1-14.
30. Goodman, G., Electrical Conductivity Anomaly in Vanadium Sesquioxide. Phys. Rev. Letters, V. 9, No. 7, Oct. 1, 1962, p 305.
31. MacKenzie, J.D., Preparation and Properties of Non-Crystalline Films. Rensselaer Polytechnic Inst., Troy, New York. Contract N00014-67-A-0117. Mar. 1969, AD 687 123.
32. Adler, D. et al., Semiconductor-to Metal Transitions in Transition-Metal Compounds. Phys. Rev., V. 155, No. 3, 15 March 1967, pp 851-860.
33. Barker, A.S., Jr. and J.P. Remeika. Optical Properties of V_2O_3 Doped with Chromium. Solid State Comm. V. 8, No. 19, Oct. 1970, pp 1521-1524.
34. Fan, J. and W. Paul. Preparation and Properties of Thin Vanadium Oxide Films (In Fr.), Le Vide, V. 25, No. 150, Nov./Dec. 1970, pp 232-243.
35. Morin, F.J., Oxides Which Show a Metal-to-Insulator Transition at the Neel Temperature. Phys. Rev. Letters, V. 3, No. 1, July 1, 1959, pp 34-36.
36. Terukov, E.I. et al., Dielectric-Metal Phase Transition in V_3O_5 . Sov. Phys. JETP, V. 46, No. 6, Dec. 1977, pp 1160-1167.
37. Okinaka, H., et al., Electrical Properties of V_8O_{15} Single Crystal. Phys. Letters, V. 33A, No. 6, Nov. 30, 1970, pp 370-371.
38. Abrahams, S.C., Magnetic and Crystal Structure of Titanium Sesquioxide. Phys. Rev., V. 130, No. 6, 15 June 1963, pp 2230-2237.
39. Honig, J.M., Nature of the Electrical Transition in Ti_2O_3 . Rev. of Mod. Phys., V. 40, No. 4, October 1968, pp 748-751.
40. Yahia, J. and H.P.R. Frederikse. Electrical Conduction in p-type Titanium Sesquioxide. Phys. Rev., V. 123, No. 4, Aug. 15, 1961, pp 1257-1261.
41. Bartholomew, R.F. and D.R. Frankl. Electrical Properties of Some Titanium Oxides, Phys. Rev., V. 187, No. 3, 15 Nov. 1969, pp 828-833.

42. Keys, L.K. and L.N. Mulay, Magnetic Studies of the Semiconductor to Metal Transitions in Ti_3O_5 and Ti_2O_3 . *Applied Phys. Letters*, V. 9, No. 6, 15 Sept. 1966, pp 248-250.
43. Keys L.K. and L. N. Mulay. Magnetic Susceptibility Measurements of Rutile and the Magneli Phases of the Ti-O System. *Phys. Rev.*, V. 154, No. 2, 10 February, 1967, pp 453-456.
44. Janninck, R.F. and D.H. Whitmore. Electrical Conductivity and Thermoelectric Power of Niobium Oxide. *J. Phys. Chem. Solids*, V. 27, 1966, p 1183.
45. Barker, A.S. Jr. and J.P. Remeika. Infrared Band Gap at the Metal-Nonmetal Transition in NiS. *Phys. Rev. B.*, V. 10, No. 3, 1 August 1974, pp 987-994.
46. Mattheiss, L.F., Band Model for the Metal-Semiconductor Transition in NiS. *Phys. Rev. B.*, V. 10, No. 3, 1 August 1974, pp 995-1005.
47. Ohtani, T., et al., Impurity Effects on the Metal-Semiconductor Transition in NiS. *Phys. Stat. Sol. (b)*, V. 66, 1974, pp 765-772.
48. Adler, D., Insulating and Metallic States in Transition Metal Oxides. *Solid State Physics-Advances in Research and Applications*, Edited by: Seitz, F. et al., V. 21, 1968, Academic Press, New York and London, pp 1-113.
49. Samuelson, E.J., et al., Neutron Scattering from Magnetite Below 1190K. *J. Appl. Phys.*, V. 39, No. 2, 1 Feb. 1968, pp 1114-1115.
50. Rogers, D.B., et al., Crystal Chemistry of Metal Dioxides with Rutile-Related Structures. *Inorganic Chemistry*, V. 8 No. 4 April 1969, pp 841-849.
51. Penney, T., et al., Insulator-Metal Transition and Long-Range Magnetic Order in EuO. *Phys. Rev. B.*, V. 5, No. 9, 1 May 1972, pp 3669-3674.
52. Jorgenson, G.V., et al., SMATH Nonlinear (Part II)-Advanced Development of Nonlinear Materials (U). Final Report AFWAL-TR-80-4101, Part II, Honeywell Inc., Minneapolis, MN January 1981, Report Secret, Classified by: DD254 dtd 31 Jan. 1979 and Multiple Sources; Declassify on: 31 Dec. 1992.
53. Hebb, M.H., Electrical Conductivity of Silver Sulfide. *J. Chem. Phys.*, V. 20, No. 1, January 1952, pp 185-190.
54. Nyberg, G.A. and R.A. Buhrman. Summary Abstract: Preparation and Optical Properties of Reactively Evaporated VO_2 Thin Films. *J. Vac. Sci. Technol.*, V. A2(2), Apr.-June 1984, pp 301-302.

55. Kristensen, I. K., Semiconductor-to-Semiconductor Transition in the Pseudobinary System $\text{TiO}_2\text{-VO}_2$. J. Appl. Phys., V. 39, 1968, pp 5341-5342.
56. MacChesney, J.B. and H.J. Guggenheim. Growth and Electrical Properties of Vanadium Dioxide Single Crystals Containing Selected Impurity Ions. J. of Phys. and Chem. of Solids, V. 30, No. 2, Feb. 1969, pp 225-234.
57. Rao, C.N.R., et al., Phase Transitions and Conductivity Anomalies in Solid Solutions of VO_2 with TiO_2 , NbO_2 and MoO_2 . J. of Phys. and Chem. of Solids, V. 32, No. 6, 1971, pp 1147-1150.
58. Goodenough, J.B., The Two Components of the Crystallographic Transition in VO_2 . J. Solid State Chem., V. 3, 1971, pp 490-500.
59. Villeneuve, G., et al., Contribution to the Study of the Metal-Insulator Transition in the $\text{V}_{1-x}\text{Nb}_x\text{O}_2$ System: I-Crystallographic and Transport Properties. J. Phys. Chem. Solids, V. 33, 1972, pp 1953-1959.
60. Reyes, J.M., et al., Transport Properties of Tungsten-Doped VO_2 . Can. J. Phys., V. 54, 1976, pp 408-412.
61. Nygren, M. and M. Israelsson. A D.T.A. Study of the Semiconductor-Metallic Transition Temperature in $\text{V}_{1-x}\text{W}_x\text{O}_2$, $0 \leq x \leq 0.067$. Mat. Res. Bull., V. 4, 1969, pp 881-886.
62. Hörlin, T., et al., Electrical and Magnetic Properties of $\text{V}_{1-x}\text{W}_x\text{O}_2$, $0 \leq x \leq 0.060$. Mat. Res. Bull., V. 7, 1972, pp 1515-1524.
63. Fukuma, M., et al., Preparation of VO_2 Thin Film and Its Direct Optical Bit Recording Characteristics. Appl. Optics, V. 22, No. 2, 15 January 1983, pp 265-268.
64. Goodenough, J.B. and H.Y-P. Hong. Structures and a Two-Band Model for the System $\text{V}_{1-x}\text{Cr}_x\text{O}_2$. Phys. Rev. B., V. 8, No. 4, 15 August 1973, pp 1323-1331.
65. Greenberg, C.B., Undoped and Doped VO_2 Films Grown from $\text{VO}(\text{OC}_3\text{H}_7)_3$. Thin Solid Films, V. 110, 1983, pp 73-82.
66. Futaki, H. and M. Aoki. Effects of Various Doping Elements on the Transition Temperature of Vanadium Oxide Semiconductors. Jap. J. Appl. Phys., V. 8, No. 8, August 1969, pp 1008-1013.
67. Bayard, M.L.F., et al., Preparation and Properties of the Oxyfluoride Systems $\text{V}_2\text{O}_5\text{-xF}_x$ and $\text{VO}_2\text{-xF}_x$. J. Solid State Chem., V. 3, 1971, pp 484-489.

68. Chamberland, B.L., The Hydrothermal Synthesis of $V_2O_4-xF_x$ Derivatives. Mat. Res. Bull., V. 6, 1971, pp 425-432.
69. Sakata, K., Study of the Phase Transition in $Nb_xTi_{1-x}O_2$. J. Phys. Soc. Japan, V. 26, 1969, p 1067.
70. Duchene, J., et al., R.F. and D.C. Reactive Sputtering for Crystalline and Amorphous VO_2 Thin Film Deposition. Thin Solid Films, V. 12, 1972, pp 231-234.
71. McWhan, D.B., et al., Mott Transition in Chromium doped V_2O_3 . Phys. Rev. Letters, V. 23, No. 24, Dec. 1969, pp 1384-1387.
72. Minomura, S. and H. Nagasaki. The Effects of Pressure on the Metal-to Insulator Transition in V_2O_4 and V_2O_3 . Phys. Soc. of Japan, J., V. 19, No. 1, Jan. 1964, pp 131-132.
73. Neuman, C.H., et al., Pressure Dependence of the Resistance of VO_2 . J. of Chem Phys., V. 41, No. 6, Sept. 1964, pp 1591-1595.
74. Howe, A.T. et al., Fabrication of Films of Hydrogen Uranyl Phosphate Tetrahydrate and Their Use as Solid Electrolytes in Electrochromic Displays. Thin Solid Films, V. 67, 1980, pp 365-370.
75. Green, M., et al., A Thin Film Electrochromic Display Based on the Tungsten Bronzes. Thin Solid Films, V. 38, 1976, pp 89-100.
76. Goldner, R.B., et al., High Near-Infrared Reflectivity Modulation with Polycrystalline Electrochromic WO_3 Films. Appl. Phys. Lett., V. 43, No. 12, 15 December 1983, pp 1093-1095.
77. Colton, R.J., et al., Electrochromism in Some Thin-Film Transition-Metal Oxides Characterized by X-ray Electron Spectroscopy. J. Appl. Phys., V. 49, No. 1, January 1978, pp 409-416.
78. Holloway, P.H. and R.E. Hummel. Electrically Controlled Coloration of Materials. DTIC Technical Report AD A071717, June 1979.
79. Chang, I.F. and W.E. Howard. Performance Characteristics of Electrochromic Displays. IEEE Trans. Electron Devices, V. ED-22, No. 9, Sept. 1975, pp 749-758.
80. Blanc, J. and D.L. Staebler. Electrocoloration in $SrTiO_3$: Vacancy Drift and Oxidation-Reduction of Transition Metals. Phys. Rev. B., V. 4, No. 10, 15 November 1971, pp 3548-3557.

81. Dautremont-Smith, W.C., Transition Metal Oxide Electrochromic Materials and Displays: A Review. Part 2. Displays, V. 3, No. 2, April 1982, pp 67-80.
82. Shay, J.L. and G. Beni. Anodic Iridium Oxide Films: A New Electrochromic. Publ. by IEEE in: Conference Record of the 1978 Biennial Display Research Conference, 1978, pp 30-33.
83. Schoot, C.J., et al., New Electrochromic Memory Display. Appl. Phys. Letters, V. 23, No. 2, 15 July 1973, pp 64-65.
84. Kaufman, F.B., et al., Polymer-Modified Electrodes: A New Class of Electrochromic Materials. Appl. Phys. Letters, V.36, No. 6, 15 March 1980, pp 422-425.
85. Nicholson, M.M. and T.P. Weismuller. Multicolor Electrochromic Display Technology. Proc. of the IEEE 1983 National Aerospace and Electronics Conference (NAECON 1983), V. 1, pp 368-374.
86. Gazard, M., et al., Electrooptical Properties of Thin Films of polyheterocycles. Journal de Physique, Colloque C3, supplement au n06, Tome 44. Juin 1983, pp C3-537 to C3-542.
87. Vezzoli, G.C., On-State Decay in NbO₂: Relationship to Recombination and to Nonlinear I-V. J. Appl. Phys., V. 51, No. 5, May 1980, pp 2693-2695.
88. Shin, S.H., et al., High-Speed High-Current Field Switching of NbO₂. J. Appl. Phys., V. 48, No. 7, July 1977, pp 3150-3153.
89. Kittel, C. Introduction to Solid State Physics. 3rd Edition. John Wiley and Sons, Inc. New York, London, Sydney. December 1968.

ADDITIONAL REFERENCES

1. Mansingh A. and Singh, R., Low Frequency Dielectric Relaxation in Lightly Doped VO_2 Single Crystals. J Phys. Chem. Solids, Vol. 45, No. 1, 1984, pp.79-88.
2. Zylbersztejn, A., et al., Fast Pulse Measurements of the Dielectric Constant of Semiconducting VO_2 . Physics Letters, Vol. 54A, No. 2, 25 August 1975, pp.145-147.
3. Polovov, V.M., et al., M.P., Thermodynamics of the semiconductor-metal transition in Ni_{1-x}S . Sov. Phys.-JETP, Vol. 43, No. 1, January 1976, pp.78-82.
4. Reyes, J.M., et al., Transport Properties of Impurity-Doped VO_2 . Can. J. Phys., Vol. 54, 1976, pp.413-423.
5. Heinrich, A., et al., IR-Absorption in Doped and Undoped VO_2 . Phys. Stat. Sol. (a) 72, 1982, pp.K61-K64.
6. Kimizuka, N., et al., Behavior of Vanadium Dioxide Single Crystals Synthesized Under the Various Oxygen Partial Pressures at 1500 K. Journal of Solid State Chemistry, Vo. 9, 1974, pp. 69-77.
7. Kapaev, V.V. and R. Kh Timerov, The Dynamics of Thermal Switching in a Medium with A Dielectric - Metal Phase Transition. Mikroelektronika, Vol. 5, No. 4, July-August, 1976, pp. 338-343.
8. Cuomo, J.J., et al., Electrochemical, RuO_2 -Based Light Switch. IBM Technical Disclosure Bulletin, Vol. 24, No. 1B, June 1981.
9. Dixit, V.G. and K., Singh, Electrical Conductivity of Transition Metal Oxide Glasses in the System $\text{V}_2\text{O}_5\text{-B}_2\text{O}_3\text{-TeO}_2$ at High Temperatures. J. Phys. Chem. Solids, Vol. 44, No. 9, 1983, pp. 859-864.

10. Gridnev, S.A., et al., Influence of Defects on the Switching of the Pure Intrinsic Ferroelastic $\text{KH}_2(\text{SeO}_3)_2$. Bull Acad. Sci. USSR, Phys. Ser. (USA), Vol. 47, No. 3, 1983, pp.75-77.
11. Sawant, S.R., R.N., Patil, Cation Distribution Magnetisation and Electrical Switching in $\text{Cu}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ System. Indian J. Phys., 56A, 233-238, 1982.
12. Chang, I.F., State of The Art of Electrochromic and Electrochemichromic Displays. Electro/81, Conference Record, 14/2/1-5, 1981, Conf. held 7-9 April 1981, N.Y. Publ. by Ecktron, Conventions, El Segundo, CA.
13. Molnar, B.J., et al., Electrochromism in WO_3 films with BaO Additions. J. Vac. Sci. Technol. 15(2) March/April 1978, pp.261-263.
14. Dimitriev, Y., et al., Bipolar Threshold Switching in Vanadate Glasses. Int. J. Electronics, Vol. 50, No. 5, 1981, pp.385-394.
15. Burgelman, M., A Model for the Off-On Transition in Thin ZnTe Films. Appl. Phys. 21, 1980, pp.249-255.
16. Freller, H., et al., Electrochromic Displays, Siemens, A.G., Research Report T81-141, August 1981.
17. Dautremont-Smith, W.C., Transition Metal Oxide Electrochromic Materials and Displays: a Review, Part 1: Oxides with Cathodic Coloration. Displays. January 1982, pp.3-23.
18. Vezzoli, G.C., et al., Threshold Switching Polycrystalline NbO_2 : Decay and Recovery of the On State at Room and Low Temperatures and its Relationship to Trapping Centers. J. Appl. Phys. 54 (10), October 1983, pp.5828-5838.
19. Vezzoli, Gary C., Recovery Curve for Threshold-Switching NbO_2 . J. Appl. Phys. 50 (10), October 1979, pp.6390-6395.

20. Baur, G., et al., Investigation of Electrochromic Effects for Display Application. National Technical Information Service, Document No. PB83-112845, (1982).
21. Freller, H., Electrochromic Displays. National Technical Information Service, Document No. PB82-112202, (December 1979).
22. Neal, W.H. II, et al., A Study of Nucleation and Dynamic Phenomena of Thermal Filaments in Vanadium Dioxide. Defense Technical Information Center, Document No. AD-774528, (12 September 1973)..
23. Deb, S.K. and H., Witzke, H., Electrochromic Display Device. Defense Technical Information Center, Document No. AD-A02725.
24. Gittleman, J. and E.K., Sichel, Granular Optical Materials. Defense Technical Information Center, Document No. AD-A054099.
25. Rast, H.E., Electrochromic Optical Mask and Method of Fabrication. Patent Application. Defense Technical Information Center, Document No. AD-D005967..
26. Lalevic, B., Solid State Switches. National Technology Information Center, Document No. AD-D000718, (12 February 1975).
27. Nicholson, M.M. and R.V., Galiardi, Investigation of Lutetium Diphthalocyanine as an Electrochromic Display Material. Defense Technical Information Center, Document No. AD-A039596, (May 1977).
28. Fuschillo, N. and B. Lalevic, Transport, Dielectric and Switching Properties of Transition Metal Oxides. National Technical Information Center, Document No. AD-001842.
29. Wild, R.L., et al., Thermochromism and Electrical Conductivity in Doped SrTiO₃. Defense Technical Information Center, Document No. AD-773343.
30. Holloway, P.H., Electrically Controlled Coloration of Materials. Defense Technical Information Center, Document No. AD-A133420.

31. Crosby, G.A., Luminescent Transition Metal Complexes in Magnetic and Electric Fields. Defense Technical Information Center, Document No. AD-A021108.
32. Exarhos, G.J., et al., Resonance Raman Study of the Reversible Thermochemical Phase Transition of a Polydiacetylene. Defense Technical Information Center, Document No. AD-783709.
33. Eckels, D.E., The Visual Effects of Switching 0.15 AS-0.12Ge-0.73Te Glass. Thesis in Physics Department at Iowa State University, Ames Laboratory. Document No. IS-T-590, (December 1973).
34. Braunstein, R., Electrochromic Glasses. Defense Technical Information Center. Document No. AD-A091641.
35. Kennedy, T.N., F.M., Collins, A Vanadium Oxide Film "Switching" Element. Defense Technical Information Center, Document No. AD-683368.
36. Mattis, D.C., Problems in Polyconductivity: The Insulator-Metal Transition. Defense Technical Information Center, Document No. AD-701636.
37. Richtol, H.H. and R.L., Strong, The Photochemistry and Optical Rotatory Dispersion of Photochromic Biantrenes. Defense Technical Information Center, Document No. AD-704958.
38. Braunstein, R. and I. Lefkowitz, Ferroelectric, Photochromic, and Electrochromic Glasses. Ferroelectrics, Vol. 27, 1980, pp. 225-230.
39. Takahashi, T. and O., Yamada, Electrical Switching in Cadmium Boracite Single Crystals. IEEE Proc. of the Conf. on High Temperature Electronics, 1981, pp.67-70.
40. Livage, J., Amorphous Transition Metal Oxides. Journal De Physique. October 1981, pp.C4-981 to C4-991.

41. Potember, R.S., et al., Erasable Optical Switching in Semiconductor Organic Charge-Transfer Complexes. Journal de Physique, June 1983, pp.C3-1597 to C3-1604.
42. Laplante, P.R., MOX Multi-Layer Switching Device Comprising Niobium Oxide. U.S. Patent No. 4,118, 727. October 3, 1978.

APPENDIX A

MATERIALS SCREENING TESTS

As part of a contract supported by the U.S. Air Force, Honeywell Systems and Research Center developed an experimental procedure for screening materials that might exhibit semiconductor-to-metal (SCM) transitions or that might have nonlinear refractive index shifts. This section gives a discussion of that development and the results obtained through using the developed procedure.

Semiconductor-to-Metal Transitions

Magnetic order strongly affects free carrier motion. In an antiferromagnetic semiconductor, there is an energy advantage for the conduction electrons to self-localize into a region that becomes ferromagnetic due to the presence of the large number of electrons. If the carrier density is not too large, these ferromagnetic regions will exist as a periodic structure within the antiferromagnetic matrix. The conductivity of this composite will be low since the conduction electrons are localized in the ferromagnetic structure.

As the Neel temperature is reached, there will be a rapid rise in the number of conduction electrons as the ferromagnetic regions and antiferromagnetic structures dissolve. To obtain a semiconductor-to-metal transition at the Neel temperature, the free conduction electrons need to be able to move easily within the crystal. This requires a high mobility conduction band such as is formed by the overlap of d orbitals. Compounds of the form MX (where M is a transition metal and X is S, Se, Te, As, Sb, or P) which have the NiAs crystal structure commonly are antiferromagnetic with unfilled d orbitals. Thus, many materials of the form MX were evaluated in our search for materials displaying semiconductor-to-metal transitions.

Nonlinear Refractive Index Transformation

There are several types of nonlinear behavior which do not result in the band gap collapse that is characteristic of semiconductor-to-metal phase transitions. These other transformations lead to less drastic changes in optical properties, namely a refractive index shift. Such a change is usually small and will not, of itself, significantly alter the optical properties of a single film of material. These

materials can become very effective when used as components in an optical coating system. For example, if such materials are used as elements in multilayer stacks of quarter wave optical layers, small index changes caused by a nonlinear transition can result in large spectral reflectance changes. That kind of an application does not appear to be of interest to this program on buildings energy applications. However, we include the results of the screening tests for completeness sake, and because there could develop a use for such materials in a related energy technology.

Experimental Procedure for Evaluating Candidate Nonlinear Materials

Single crystals or polycrystalline samples of candidate materials (large enough to perform optical measurements) would be quite expensive. Thus, it was decided that the cost and time required to obtain single-crystal or polycrystalline samples should be expended on only those materials that had been shown to display temperature dependent dielectric properties. Since most materials can be obtained relatively inexpensively, in powder or chunk form, our screening techniques were designed for evaluating powders or small chunks of material.

We used a two-step screening process. The first step involved a measurement of the dielectric constant and loss tangent (at 1 kHz) as a function of temperature. Materials that displayed temperature dependent properties at 1 kHz were then evaluated at 21 GHz by measuring their microwave transmission as a function of temperature. Materials that showed temperature dependent properties at both 1 kHz and 21 GHz were prepared as coatings or crystals for an evaluation of the temperature dependence of their optical properties.

The screening procedure was based on the frequency dependence of the contributions to the polarizability (α) of a material. The dielectric constant (ϵ) is related to the total polarizability per molecule as follows:

$$\epsilon = 1 + \sum_{n=1}^{\infty} (4)^{n-1} \cdot (12) \left(\frac{\pi \rho L \alpha}{3M} \right)^n \quad (1)$$

The dielectric constant also shows the same general frequency dependence as α . In Equation (1), M is the molecular weight, ρ is the density, L is Avogadro's number, and α is the total polarizability per molecule.

Figure A-1 shows the frequency dependence of the polarizability. As indicated, α is a sum of electronic, ionic, and orientational contributions. At low electromagnetic radiation frequencies, all three contributions respond and influence the dielectric properties of the material. However, as the frequency increases, those contributions with low resonant frequencies become ineffective so that in the infrared and visible regions only the electronic, and possibly the ionic contributions, are effective. Thus, if a material does not have temperature dependent dielectric properties at low frequencies, the dielectric properties in the visible and IR will also be temperature independent since the low frequency properties are influenced by all the contributions. However, if the dielectric properties of a material are temperature dependent at low frequencies, one of two situations is possible:

1. The temperature dependence is a result of low resonant frequency contributions which will not affect the visible and IR properties, or
2. The temperature dependence is a result of higher resonant frequency contributions which could affect the optical properties.

The second step in the screening procedure involved microwave transmission measurements through the material as a function of temperature. If no temperature dependence of the microwave transmission was noted, the material was dropped from further consideration. However, if a temperature dependent microwave transmission was present, the material was considered a candidate for screening tests at optical frequencies.

Experimental Results

The results of screening tests of candidate nonlinear materials are shown in Table A-1. Candidate materials for both nonlinear semiconductor-to-metal transitions and nonlinear refractive index changes are listed. Temperatures listed in Table A-1 could be as much as 20 degrees greater than the actual temperature of the materials because the

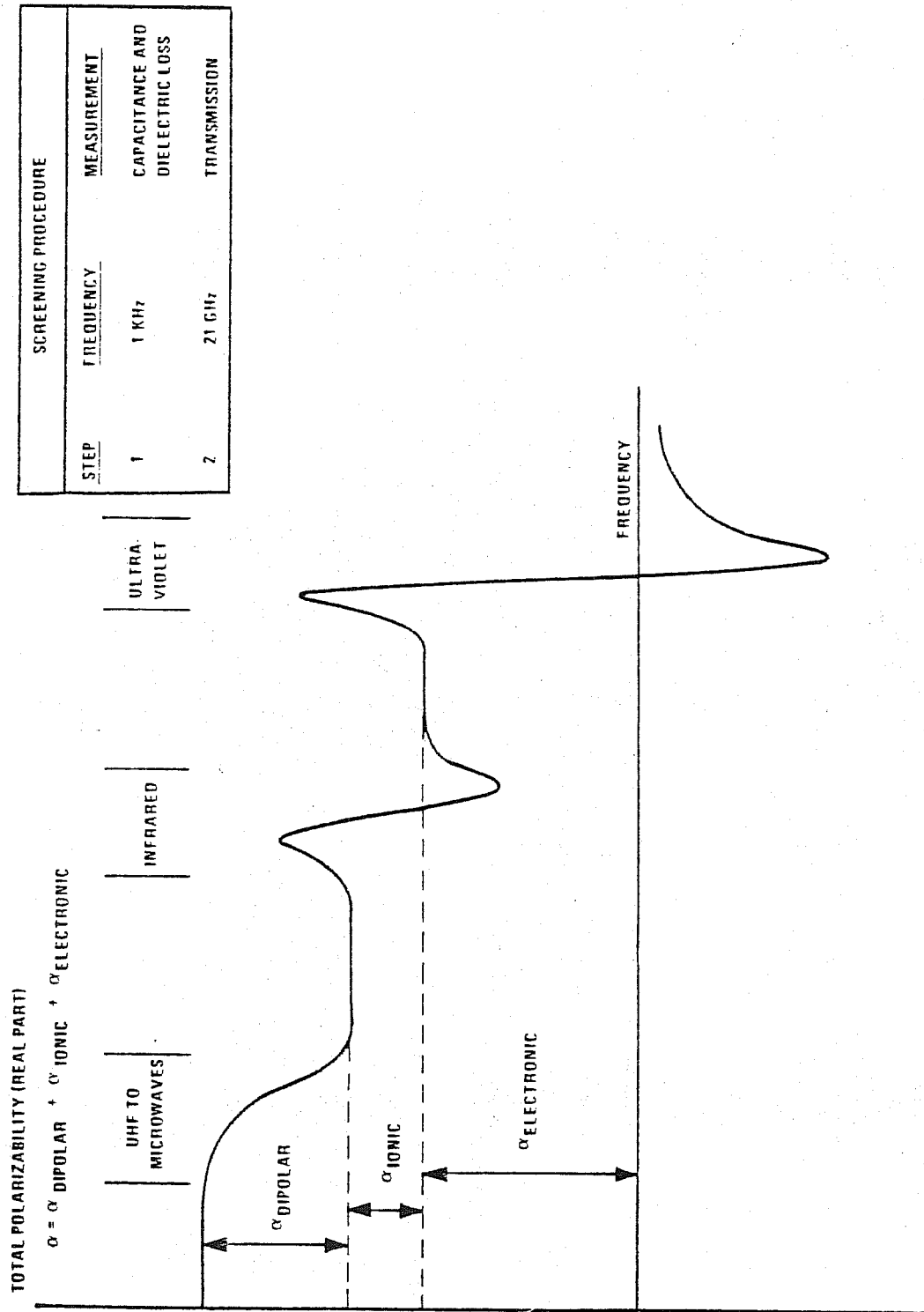


Figure A-1. Dielectric Constant and Polarizability

Table A-1. SCREENING TEST RESULTS: TEMPERATURE DEPENDENCE OF DIELECTRIC PROPERTIES

MATERIAL	FREQUENCY = 1 KHz		FREQUENCY = 21 GHz
	DIELECTRIC CONSTANT	DIELECTRIC LOSS	TRANSMISSION
AgI (2)	INCREASES BY FACTOR OF 10^2 AT $\geq 140^\circ\text{C}$	NO ABRUPT CHANGE	DECREASES BY FACTOR OF ~ 80 AT $\geq 160^\circ\text{C}$
As ₂ S (1)	INCREASES BY FACTOR OF 10^4 AT $\geq 120^\circ\text{C}$	INCREASES BY FACTOR OF $\sim 10^2$ AT $\geq 120^\circ\text{C}$	NOT TESTED YET
CoS ₂ (1)	DECREASES BY FACTOR OF 100 AT $\geq 110^\circ\text{C}$	DECREASES BY FACTOR OF 10 AT $\geq 110^\circ\text{C}$	NO ABRUPT CHANGE FOR
CoSe (1)	NO ABRUPT CHANGE	NO ABRUPT CHANGE	---
CoTe (1)	DECREASES BY FACTOR OF ~ 2 AT $\geq 40^\circ\text{C}$	DECREASES BY FACTOR OF 10 AT $\geq 40^\circ\text{C}$	NOT YET TESTED
Cu ₂ S (1)	INCREASES BY FACTOR OF ~ 3 AT $\geq 130^\circ\text{C}$	NO ABRUPT CHANGE	NOT TESTED YET
FeS (1)	INCREASES AT $\geq 140^\circ\text{C}$	INCREASES AT $\geq 140^\circ\text{C}$	NOT TESTED YET
FeSb ₂ (1)	INCREASES BY FACTOR OF ~ 500 AT $\geq 90^\circ\text{C}$	INCREASES BY FACTOR OF 100 AT $\geq 90^\circ\text{C}$	NO ABRUPT CHANGE
FeSe (1)	NO ABRUPT CHANGE	NO ABRUPT CHANGE	
HfSe ₂ (1)	NO ABRUPT CHANGE	NO ABRUPT CHANGE	
HgI ₂ (2)	NO ABRUPT CHANGE	INCREASES BY FACTOR OF ~ 10 AT $\geq 100^\circ\text{C}$	DECREASES BY FACTOR OF 10 AT $\geq 130^\circ\text{C}$
In ₂ Se ₃ (2)	NO ABRUPT CHANGES AT $\leq 180^\circ\text{C}$		DECREASES BY FACTOR OF 20 AT $\geq 200^\circ\text{C}$
MgTe (1)	NO ABRUPT CHANGE AT $< 180^\circ\text{C}$	NO ABRUPT CHANGE AT $< 180^\circ\text{C}$	---
MuS ₂ (1)	INCREASES BY FACTOR OF 5 AT $\geq 100^\circ\text{C}$	NO ABRUPT CHANGE	---
NiSe (1)	NO ABRUPT CHANGE AT $< 180^\circ\text{C}$	INCREASES BY FACTOR OF 30 AT $\geq 110^\circ\text{C}$	NOT TESTED YET
NiTe (1)	NO ABRUPT CHANGE AT $< 180^\circ\text{C}$	NO ABRUPT CHANGE AT $< 180^\circ\text{C}$	---
TaS ₂ (1)	NO ABRUPT CHANGE	DECREASES BY FACTOR OF 4 AT $\geq 40^\circ\text{C}$	NOT TESTED YET
TlI (2)	NO ABRUPT CHANGES AT $< 180^\circ\text{C}$	NO ABRUPT CHANGES AT $< 180^\circ\text{C}$	ABRUPT CHANGE AT $\geq 200^\circ\text{C}$
ZrSe ₂ (1)	NO ABRUPT CHANGE	NO ABRUPT CHANGE	---
ZrTe ₂ (1)	NO ABRUPT CHANGE	NO ABRUPT CHANGE	---

- (1) Candidate semiconductor-metal transition material
 (2) Candidate refractive index change material

thermocouple could not be inserted directly into the material without affecting the measurements. At that stage we were mainly interested in whether a change in properties occurred as the temperature was varied. More exact measurements of the transition temperature could be made later on those materials that showed nonlinearities at optical frequencies.

Limitations in the program schedule and funding prevented us from making microwave transmission measurements of all the materials that showed low frequency temperature dependent properties. However, of those that were evaluated at microwave frequencies, AgI, HgI₂, In₂Se₃, and TlI showed temperature dependent properties and were considered candidates for further evaluation at optical frequencies. Those four materials were candidates for thermally induced refractive index change nonlinearities. As stated previously, that type of material might not be applicable for improved energy efficiency in buildings.

One material (Ag₂S) that exhibited nonlinearities at 1 kHz, but was not tested at microwave frequency, has undergone considerable development on a subsequent Air Force contract (Ref. 52). Ag₂S has been included on the thermochromic materials matrix (Table 1).

